ACS NANO

www.acsnano.org

ARTICLE

# Printable and Versatile Superhydrophobic Paper via Scalable Nonsolvent Armor Strategy

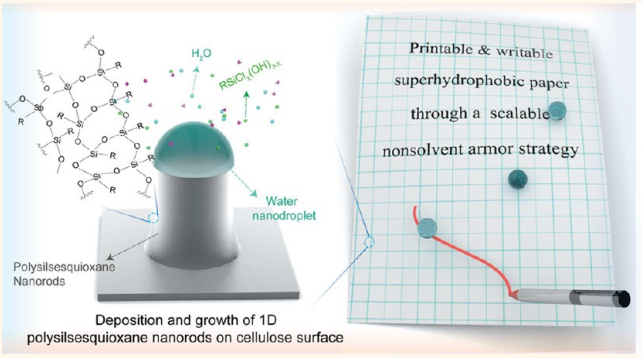
Shanqiu Liu, Kangwei Chen, Alma Salim, Jingguo Li, Davide Bottone, and Stefan Seeger*

Cite This: *ACS Nano* 2022, 16, 9442–9451

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

**ABSTRACT:** **Despite great scientific and industrial interest in waterproof cellulosic paper, its real world application is hindered by complicated and costly fabrication processes, limitations in scale-up production, and use of organic solvents. Furthermore, simultaneously achieving nonwetting properties and printability on paper surfaces still remains a technical and chemical challenge. Herein, we demonstrate a nonsolvent strategy for scalable and fast fabrication of waterproofing paper through in situ surface engineering with polysilsesquioxane nanorods (PSNRs). Excellent superhydrophobicity is attained on the functionalized paper surface with a water contact angle greater than 160°. Notably, the engineered paper features outstanding printability and writability, as well as greatly enhanced strength and integrity upon prolonged exposure to water (tensile strength ≈ 9.0 MPa). Additionally, the PSNRs concurrently armor paper-based printed items and artwork with waterproofing, self-cleaning, and antimicrobial functionalities without compromising their appearance, readability, and mechanical properties. We also demonstrate that the engineered paper holds the additional advantages of easy processing, low cost, and mechanochemical robustness, which makes it particularly promising for real world applications.**




**KEYWORDS:** *printable superhydrophobic paper, nanodroplet, in situ surface engineering, hierarchical structure, self-cleaning, antimicrobial*

As sustainable and low-cost material, cellulosic paper plays a vital role in our daily life due to its broad range of applications, such as information recording and delivery, packaging, decoration, filtration, microfluidic device fabrication, currency, as well as use in construction and industrial processes.[1−3] Owing to the monosaccharide building units, cellulosic paper features a large quantity of hydroxyl groups, resulting in its hydrophilic nature and ultralow mechanical strength in the presence of water.[4,5] Water infiltration additionally induces the migration of water-soluble ink molecules and reduces the readability of paper print. Moreover, prolonged outdoor use leads to accelerated decomposition caused by exposure to moisture, dust, and microbes in the air.[6] Hence, it is very desirable and useful to develop cellulosic paper possessing waterproofing, self-cleaning, and antimicrobial properties that do not negatively affect its innate properties, i.e., printability, writability, and mechanical performance.

Various surface-engineering techniques, such as photolithography,[7] chemical etching,[8,9] plasma treatment,[10] and nanoparticulate deposition,[11−15] have been extensively researched for the fabrication of superhydrophobic surfaces based on inorganic or organic substrates (e.g., glass, metal, and plastic).[16] However, many of those strategies cannot be simply adopted on cellulose-based paper items because cellulose can easily be damaged by either thermal or wet-chemical treatments.[17]

Recently, cellulosic papers with water-repellent property have been developed through surface modification[18−22] and spraying with fluorinated cellulose nanofibers/esters.[4,23] However, printability has not yet been implemented on these functionalized papers. The nonprintability can be attributed to the following reasons: (i) either organic solvents or water used in these processes could induce the rearrangement of cellulose fibers, often leading to a wrinkled surface and reduced mechanical performance for the treated paper, which consequently negates the paper printability and writability; (ii) conventional superhydrophobic coatings (containing fluorides

Received: March 9, 2022
Accepted: May 18, 2022
Published: May 25, 2022





https://doi.org/10.1021/acsnano.2c02382
*ACS Nano* 2022, 16, 9442−9451

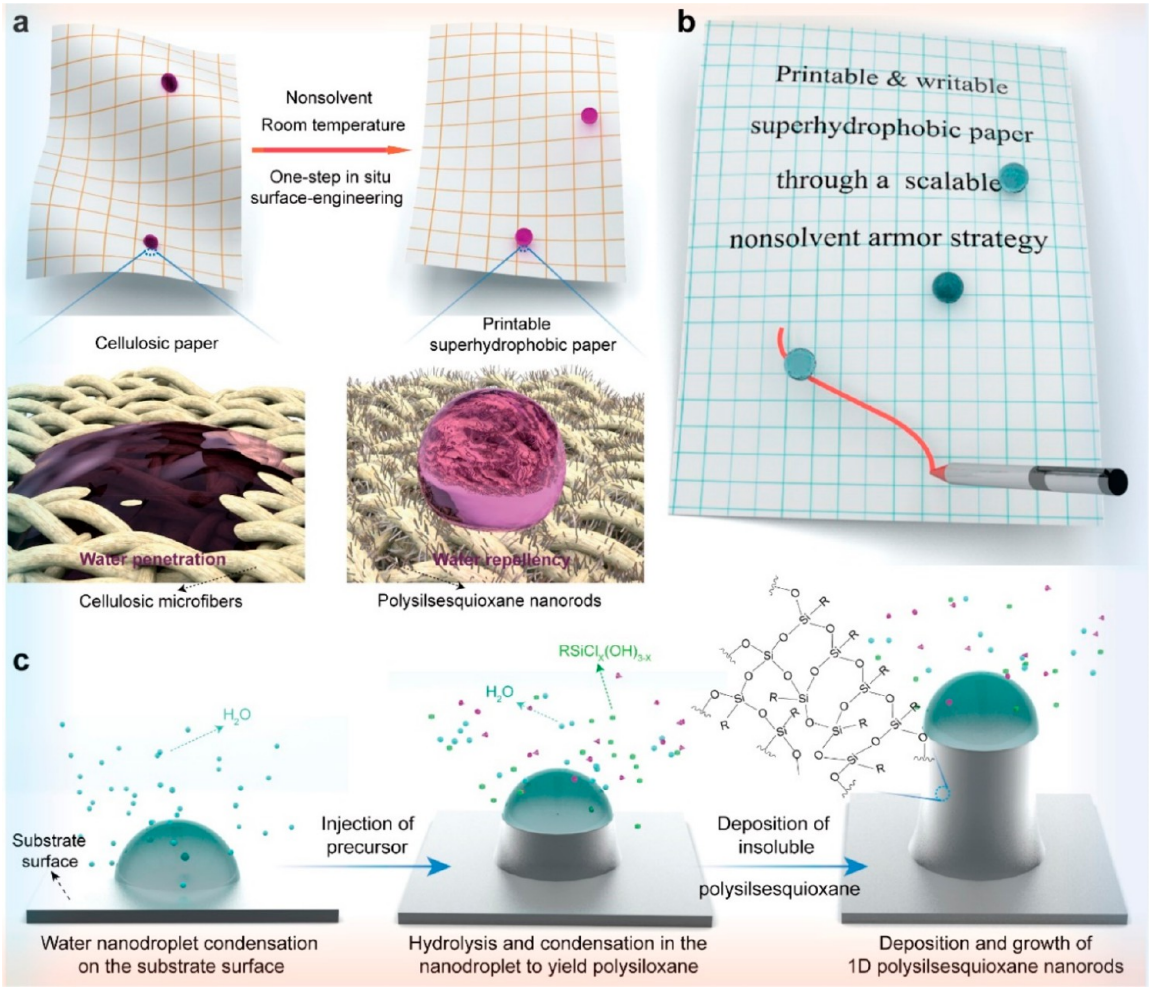



**Figure 1. Illustration of the one-step nonsolvent strategy for designing printable superhydrophobic paper. Schematics showing (a,b) preparation of printable superhydrophobic paper via in situ surface engineering of PSNRs and (c) growth mechanism of 1D PSNRs.**

or a polymer layer) feature low adhesion and wettability toward ink; (iii) in most cases, complex fabrication processes limit upscaling fabrication of such material for practical printing applications. In addition, fluorinated compounds or organic solvents involved in traditional surface modification methods are subject to environmental and safety concerns as well as cost issues.[24] Therefore, designing superhydrophobic paper that simultaneously features printability is, despite its high demand, still a challenge.

In this work, we present an unconventional strategy to fabricate printable superhydrophobic paper through surface-engineering with polysilsesquioxane nanorods (PSNRs). Being synthesized at room temperature and without solvent, potential damages occurring to the engineered paper by either heat or solvent exposure are avoided; meanwhile, environmental and safety concerns are minimized. The introduced PSNRs provide nanoscale manipulation on the surface texture as well as low surface energy, endowing the engineered paper with excellent water repellency. Importantly, unlike previously reported superhydrophobic papers or paper-like items,[4,25−27] the engineered paper features both printability and writability and could maintain its water repellency after either printing or handwriting. The incorporated PSNRs not only enhance the paper strength and durability against exposure to water but also provide the treated paper with self-cleaning and antimicrobial properties. Furthermore, as a room-temperature and solvent-free strategy, the developed approach can be applied directly on papers printed with contents, without impact on the readability and visibility of the printed characters and images. In proof-of-concept experiments, we also demonstrate that the surface-engineered PSNRs can act as transparent superhydrophobic armor for various paper-based items for outdoor use, such as advertisements and packaging materials, offering resistance toward water as well as dust and microbial contaminations, which is promising in extending the lifespan of these items. This leads to a sustainable alternative support material for outdoor advertisement and billboards and therefore reduce crude-oil-based plastic consumption.

## RESULTS AND DISCUSSION

The printable superhydrophobic paper was prepared by in situ growth of PSNRs on cellulosic paper surface through a one-step nonsolvent strategy at room temperature, as shown in Figure 1a,b. The growth mechanism of the 1D PSNRs on paper surface is illustrated in Figure 1c. Under a certain humid atmosphere, nanosized water droplets are formed due to the topographic and chemical heterogeneities of the substrate (paper) surface as well as surface tension.[28,29] These nanodroplets feature thermodynamic stability owing to the reduced chemical potential and thus act as confined reaction volumes across the whole reaction process.[30] The reaction was triggered after injection of the


https://doi.org/10.1021/acsnano.2c02382
ACS Nano 2022, 16, 9442−9451

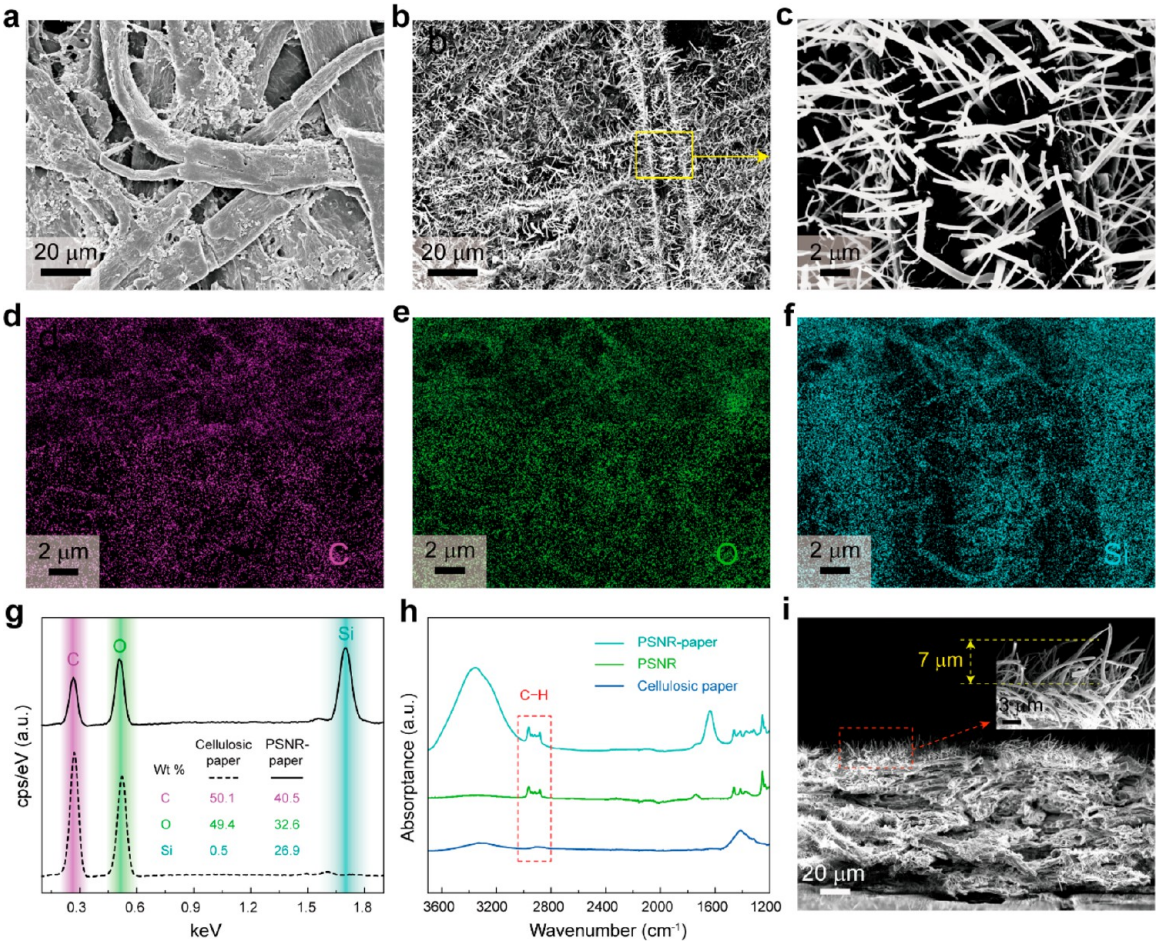



**Figure 2. Structures and chemicals evaluation of PSNR-paper and cellulosic paper. SEM images of (a) cellulosic paper and (b,c) PSNR-paper at different magnifications, as well as (d–f) corresponding EDX mapping images. (g) EDX spectra of PSNR-paper and cellulosic paper. (h) Single reflection ATR-FTIR absorbance spectra of PSNR-paper, cellulosic paper, and pure PSNR. (i) Cross-sectional SEM images of PSNR-paper.**

precursor (trichloroethylsilane). The volatile precursor reacts with water in the gas phase, yielding soluble monosilanols. Since trichloroethylsilane is more easily hydrolyzed than silanols, further hydrolysis of monosilanols to di- or trisilanols in the gas phase is unlikely. Therefore, the water droplets on the substrate surface are exposed to an atmosphere consisting of chlorosilane, water, and silanol. These silane species react progressively with the water nanodroplets present on the substrate surface via hydrolysis and condensation, resulting in the formation and deposition of insoluble polysiloxanes, which leads to the growth of one-dimensional nanorods supporting the water droplet (reaction receptacle) at their top end. Due to the presence of silanol and siloxanol species, the activity of water nanodroplets decreases and more water in the gaseous phase transports from the humid environment to the nanosized water reaction volume to sustain further reaction of hydrolysis and condensation (Figure 1c). The time-dependent morphology of PSNRs (Figure S1) agrees well with the elaborated PSNRs' growth mechanism. The reaction formulas for the hydrolysis and polycondensation of trichloroethylsilane are shown in Figure S2. Owing to the presence of hydroxyl groups on the cellulose surface, the formed PSNRs are supposed to be covalently bonded to the cellulosic paper surface through the reactive sites (−Si−Cl or −Si−OH) of silane and siloxanol species.[31]

After surface engineering with PSNRs, the functionalized paper (PSNR-paper) demonstrates a completely different surface texture at the nanoscale level in contrast to pristine cellulosic paper. To validate this, scanning electron microscopy (SEM) was used to investigate the surface morphology of the paper before and after treatment. Unlike the fibrous surface texture of cellulosic paper (Figure 2a), PSNR-paper features micro-nano hierarchical structures due to the introduced PSNR layer (Figure 2b,c). The uniform decoration of PSNRs is further confirmed by the homogeneous distribution of the Si element shown in the energy-dispersive X-ray (EDX) mapping images (Figure 2d–f).

Compared with cellulosic paper, a much higher Si content (~27 wt %) and an obvious peak corresponding to Si were observed from the EDX spectra analysis for PSNR-paper (Figure 2g). In the Fourier transform infrared (FTIR) spectra, the bands at 2950 $cm^{-1}$ and 2900 $cm^{-1}$ for the PSNR-paper are assigned to the C−H vibration of the $CH_3$ group of the decorated PSNRs,[32,33] and the same absorption bands are observed for pure PSNRs (synthesis details are shown in Materials and Methods section) (Figure 2h). These results further prove the successful decoration of PSNRs on the paper surface. The PSNR layer thickness and the average diameter of PSNRs were determined to be 7.0 $\mu$m ± 1.3 $\mu$m and 489 nm ± 71 nm, respectively, according to the analysis of cross-sectional SEM results, as shown in Figure 2i. By measuring the weight change of the cellulosic paper before and after functionalization, the


https://doi.org/10.1021/acsnano.2c02382
ACS Nano 2022, 16, 9442−9451

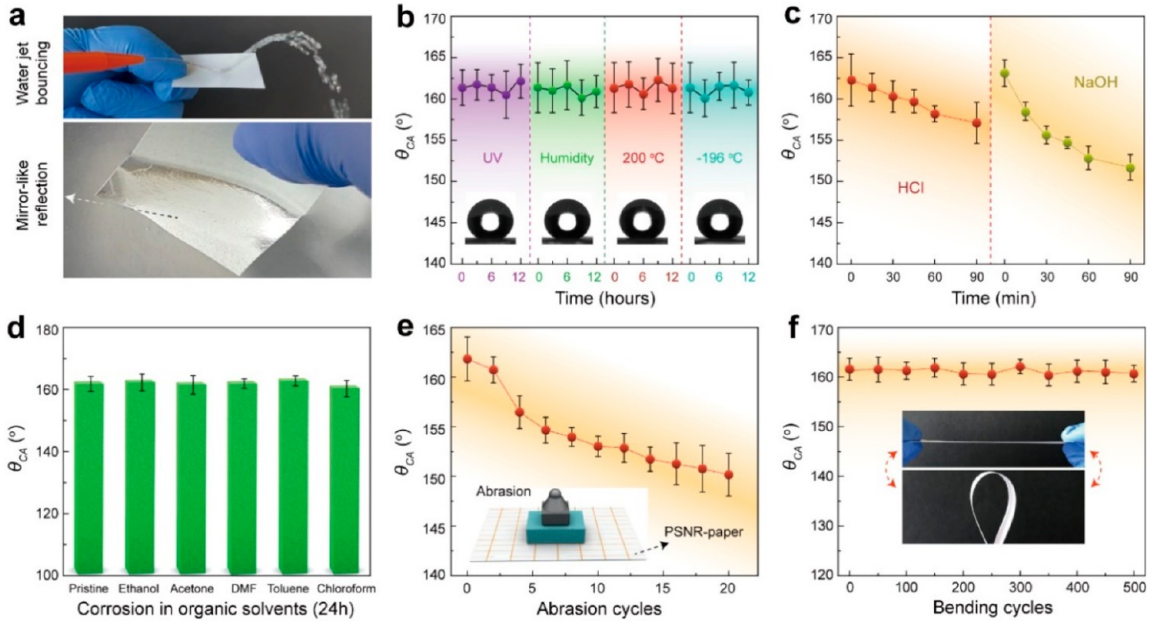



**Figure 3. Ultradurable superhydrophobicity of the PSNR-paper: (a) Water jet bounces off PSNR-paper and the mirror-like plastron layer on the surface of PSNR-paper immersed in water. (b) Durability of PSNR-paper under exposure to UV illumination, high humidity (90% RH), and extreme temperatures (200 °C and −196 °C). The inset images show the static contact angle of the water droplet after each set of tests. (c) Impact of corrosion time in HCl and NaOH on water repellency of PSNR-paper. (d) Water contact angle ($\theta_{CA}$) of PSNR-paper after 24 h corrosion from different tested organic solvents. $\theta_{CA}$ as a function of (e) abrasion and (f) bending cycles. Insets are the schemes of abrasion tests and images of bending tests.**

grafting weight percentage of PSNRs was calculated to be 19.8 wt % ± 1.1 wt %.

Due to its inherent hydrophilicity, cellulosic paper can be easily wetted and infiltrated by water (Figure S3). However, the as-prepared PSNR-paper exhibits excellent water repellency; for instance, a water jet can easily bounce off (Figure 3a and Movie S1) and water droplets show a contact angle of 162° ± 2° over its surface (Figure S3). The introduced superhydrophobicity was also demonstrated by the mirror-like plastron layer when PSNR-paper was immersed in water (Figure 3a), and the surface remained nonwetting after being taken out. This indicates the existence of a trapped air cushion between the solid paper surface and water.[24] The excellent water repellency can be ascribed to the synergic effect of the low surface energy along with the nanoscale surface roughness (Figure 2b) of the decorated PSNR layer.[34,35]

The water-repellent durability of superhydrophobic materials is an important property to be considered in practical applications. Therefore, the prepared PSNR-paper was kept under various test conditions for a predetermined time, and its wettability was periodically examined through static contact angle ($\theta_{CA}$) measurements (Figure 3b). No obvious change in $\theta_{CA}$ was observed after 12 h exposure to (i) intensive UV illumination, (ii) ultrahigh humidity (90% RH), and (iii) extreme temperatures (200 °C and −196 °C), demonstrating excellent durability of the engineered PSNR-paper. Moreover, the PSNR-paper showed outstanding stability when subjected to harsh chemical conditions. For instance, after 90 min exposure to either 0.1 M HCl or 0.1 M NaOH aqueous solution, the PSNR-paper could maintain its superhydrophobicity with $\theta_{CA}$ above 150° (Figure 3c), despite slight decreases. Interestingly, unlike most superhydrophobic surfaces,[13,36] the achieved PSNR-paper shows stable water repellency under long-term exposure to organic solvents, maintaining a final $\theta_{CA}$ of around 160 °C even after 24 h of immersion (Figure 3d). The sustained superhydrophobicity of the solvent-treated PSNR-paper was further revealed by water droplets bouncing and rolling off from the slightly titled (5°) surface (Figure S4 and Movie S2). The ultradurable water repellency of the PSNR-paper can be assigned to the physicochemical stability of the PSNR layer with which the paper surface is armored. The chemically inert low-energy surface together with the cross-linked structure of polysilsesquioxane nanorods provides excellent resistance toward chemical perturbations.[37,38] This is further demonstrated by the SEM results of the surface topology of PSNR-paper after exposure to HCl, NaOH, DMF, and toluene, as shown in Figure S5. Clearly, the PSNR layer remains intact with the paper surface after being exposed to these corrosive liquids. The collapse of the PSNRs after organic solvent treatment is ascribed to the induced capillary force during the drying process.[39,40] The retained PSNRs on the paper surface well explains the durable superhydrophobicity.

Mechanical durability of PSNR-paper was examined by abrasion and cyclic bending tests. After 20 abrasion cycles, the PSNR-paper maintained its $\theta_{CA}$ of above 150° and remained completely dry after immersion in water, indicating the sustained water repellency (Figure 3e and Figure S6). Additionally, a cyclic bending test was conducted to evaluate the flexibility and mechanical durability. Figure 3f shows the water repellency of PSNR-paper as a function of bending cycles. No visible change in $\theta_{CA}$ was observed despite 500 bending cycles. The preserved water repellency after mechanical damages can be ascribed to the maintained PSNRs protected by the microcellulose fibers during abrasion,[41] along with the residual polysilsesquioxane layer remaining on the cellulose microfibers, which is evidently revealed by the SEM images (Figure S7). These results demonstrate the mechanical durability and flexibility of PSNR-paper.



https://doi.org/10.1021/acsnano.2c02382
ACS Nano 2022, 16, 9442−9451

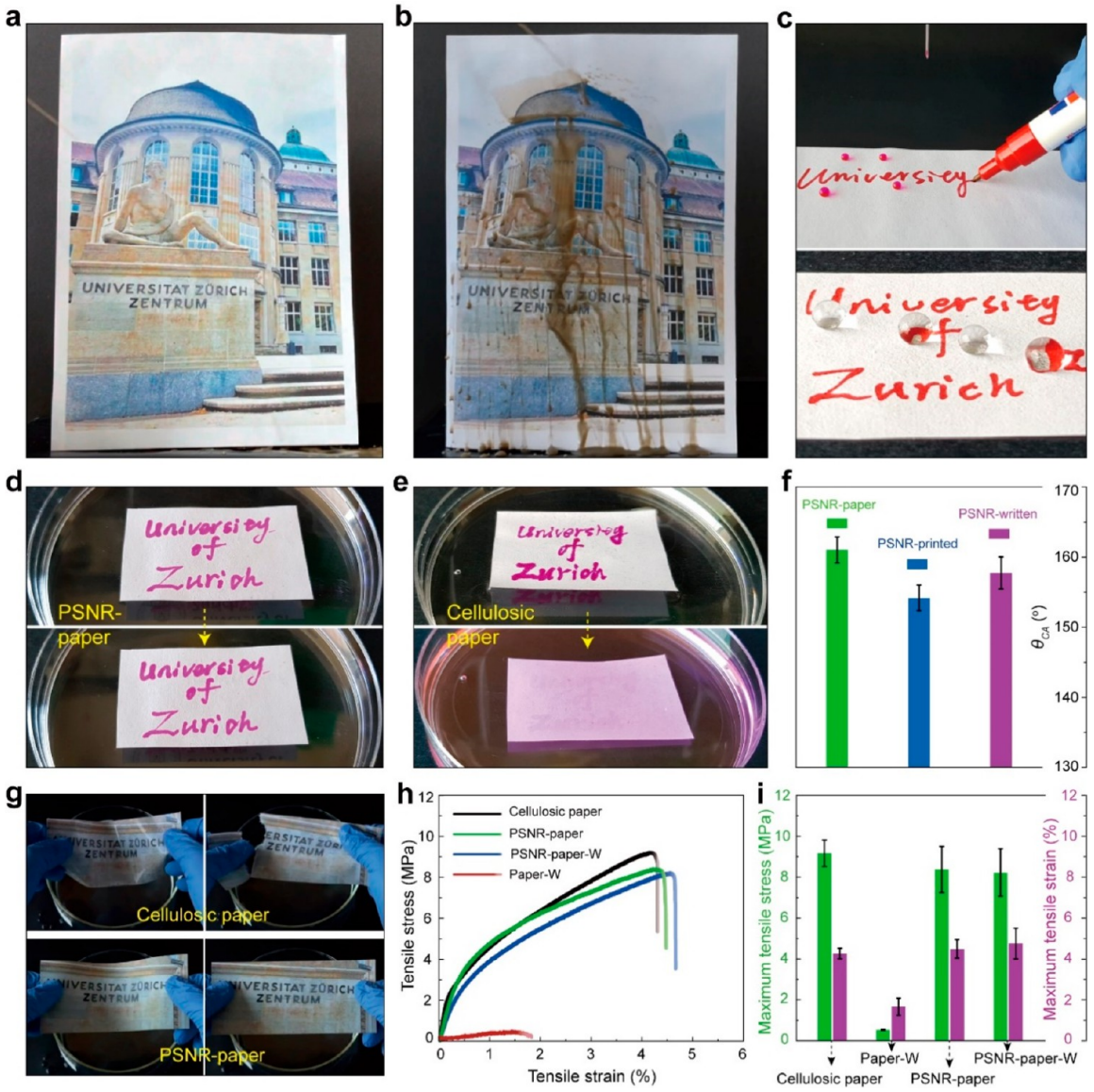



**Figure 4. Printable and writable superhydrophobic paper with enhanced integrity. Comparison of water resistance between printed (a) PSNR-paper and (b) cellulosic paper. (c) Photos showing the hand writability of PSNR-paper and its preserved superhydrophobicity after handwriting. (d) Ink written on PSNR-paper remains intact on the surface after long-term exposure to water, (e) while it diffuses easily from cellulosic paper to water. (f) $\theta_{CA}$ of PSNR-paper before and after printing and handwriting. (g) Comparison of the integrity between printed PSNR-paper and cellulosic paper after water immersion. (h) Tensile measurements and (i) maximum tensile stress and strain for printed PSNR-paper and cellulosic paper before and after water exposure. Printed PSNR-paper and cellulosic paper after exposure to water are indicated as PSNR-paper-W and paper-W, respectively.**

Notably, our strategy can be easily applied for scale-up fabrication of superhydrophobic cellulosic paper. We took commercially available paper of A4 size (297 mm × 210 mm) as the examined model. As shown in Figure S8 and Movie S3, the A4 paper armored with PSNRs exhibits excellent water repellency, as demonstrated by a water jet bouncing off its surface, whereas unmodified paper can be easily wetted and infiltrated by the water jet. Strikingly, no change was observed to the paper appearance after being engineered with PSNRs. On the contrary, a significant wrinkled surface feature was observed for the paper treated with a commonly adopted wet-chemical method (Figure S9). This is mainly caused by the stretching of cellulose fibers. When paper is soaked with the involved liquid (ethanol), the adhesion between cellulose fibers would be reduced due to liquid infiltration, causing the paper to swell, which consequently leads to the wrinkled and curled paper surface after liquid evaporation.

Unlike superhydrophobic papers reported elsewhere, the as-prepared PSNR-paper can be used directly for printing, owing to its sustained appearance and integrity after functionalization. To evaluate the printing performances, both PSNR-paper and cellulosic paper of A4 size were printed with the same content. No visible difference between the prints on PSNR-paper and cellulosic paper was found (Figure S10), indicating the outstanding printability of PSNR-paper. Importantly, the PSNR-paper even maintains its water repellency after being printed. A muddy water (10 g of soil dispersed in 200 mL of water) jet can easily bounce off the PSNR-paper printed either with pattern or text content (Figure 4a, Figure S11a, and Movie S4) and water droplets maintained nearly spherical contact on


https://doi.org/10.1021/acsnano.2c02382
ACS Nano 2022, 16, 9442−9451

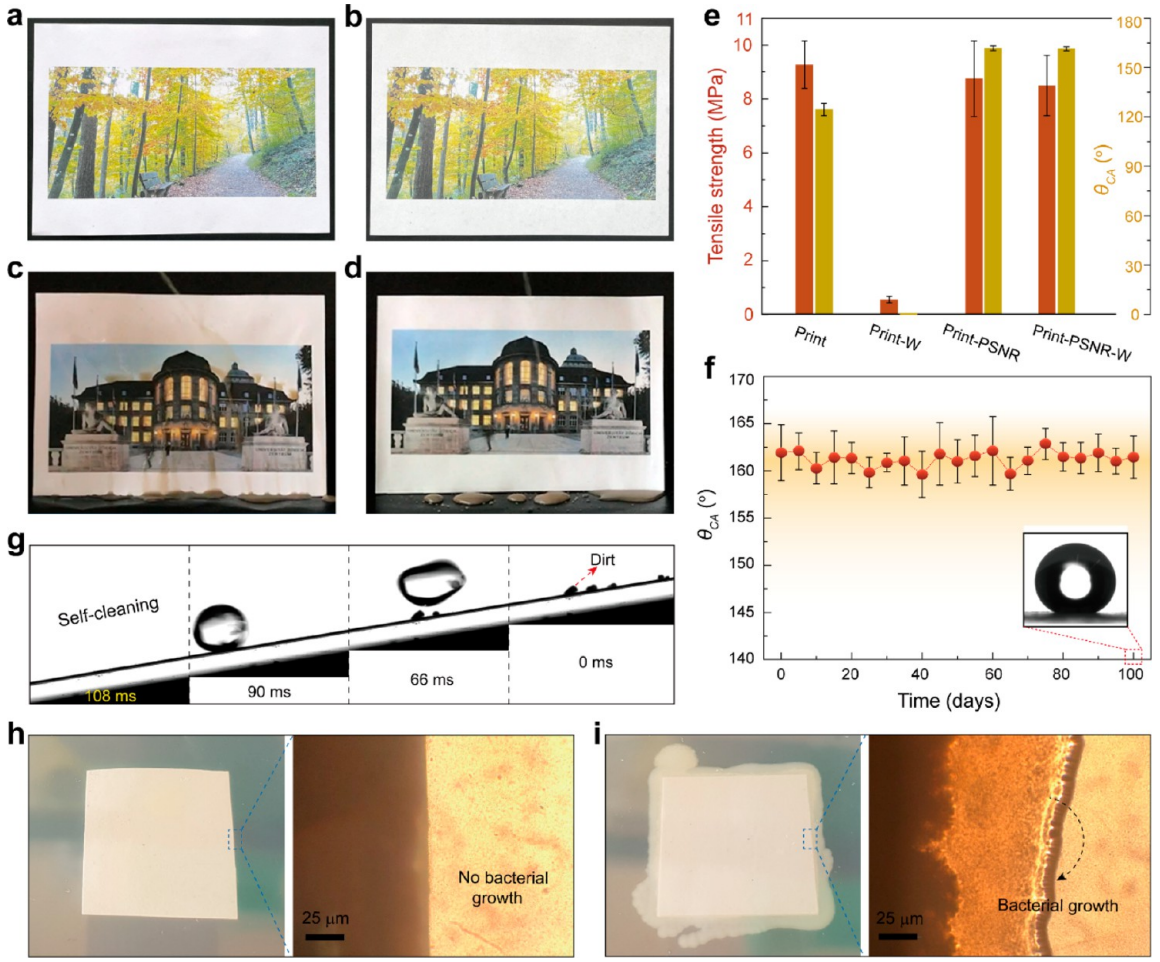



**Figure 5. Transparent superhydrophobic armor for paper-based prints. Images showing paper prints (a) before and (b) after armoring with PSNRs (print-PSNR). (c) Unmodified paper print contaminated by muddy water. (d) A jet of muddy water bounces off the print surface armored with PSNRs. (e) $\theta_{CA}$ and tensile strength for the prints (with and without PSNR-armoring) before and after water exposure. Prints armored with and without PSNRs after water exposure are indicated as print-PSNR-W and print-W, respectively. (f) Durability of the water repellency for PSNR-armored print under ambient conditions. The inset photograph shows the spherical contact of water droplet after 100 days. (g) Time-resolved images showing the self-cleaning property of PSNR-armored print after 100 days storage under ambient conditions. Comparison of antimicrobial property between (h) PSNR-armored paper and (i) cellulosic paper. Photographs in panels c and d are used with permission from University of Zurich.[42] Copyright 2010 UZH Ursula Meisser.**

the printed surface (Figure S12), demonstrating the sustained waterproof functionality of the PSNR-paper after printing. In a sharp contrast, the water jet spread and infiltrated easily while it contacted the printed cellulosic paper (Figure 4b, Figure S11b, and Movie S4).

Moreover, the PSNR-paper enables handwriting as well. Figure 4c visually shows the writability and preserved water repellency of PSNR-paper. The waterproof property of the handwritten PSNR-paper was further evaluated with ink diffusion tests. Both PSNR-paper and cellulosic paper were written with water-soluble ink (200 mg of Rhodamine B dissolved with 10 mL of ethanol) and exposed to water for a same time period (12 h). The ink on the PSNR-paper stayed intact even after long-term contact with water, whereas it dissolved into water from unmodified paper within a few seconds, as shown in Figure 4d,e, respectively.

The above results demonstrate that the PSNR-paper simultaneously possesses excellent printability, writability, as well as waterproof functionality either before or after printing and handwriting. These features can be ascribed to the introduced oleophilic and hydrophobic polysilsesquioxane nanorods on the PSNR-paper surface. The oleophilicity of PSNRs (attributed to the surface-exposed ethyl groups) together with their micro-nano rough structure results in the formation of capillary wetting and air cushion toward (oily) ink and water, respectively, which endows the PSNR-paper with both excellent ink adhesion and outstanding water repellency. The excellent affinity and adhesion of the ink toward PSNR-paper is further demonstrated by the rapid absorption and complete wetting (contact angle of 0°) of the ink on the paper surface (Figure S13). Interestingly, after handwriting/printing, the polysilsesquioxane nanorods entangled with each other (due to the capillary action of the ink) and adhered to the paper surface instead of breaking off (Figure S14). The nanorods retained on the paper surface, together with the hydrophobicity of the loaded oily ink, further confirm the waterproofing properties of the handwritten/printed PSNR-paper. The sustained superhydrophobicty of the printed and handwritten PSNR-papers was also demonstrated by the measured water contact angles above 150° (Figure 4f).

Cellulosic paper can easily get wetted by water absorption due to its hydrophilic nature and strong capillary action, thereby


https://doi.org/10.1021/acsnano.2c02382
ACS Nano 2022, 16, 9442−9451

affecting its integrity and functionality. Figure 4g shows the integrity tests for printed PSNR-paper and cellulosic paper after identical immersion time in water. PSNR-paper remained totally dry and showed high resistance toward tearing force, whereas cellulosic paper was wetted by water and was easily destroyed. To quantify the mechanical properties, tensile measurements were performed with the papers before and after water treatment (Figure 4h,i). PSNR-paper exhibits comparable tensile strength (~9.0 MPa) and stain (~4.5%) compared to pristine cellulosic paper, demonstrating that the surface-engineered PSNR layer did not compromise the mechanical properties. After exposure to water, cellulosic paper showed a significant reduction in both tensile strength and strain, indicating poor integrity. As a sharp contrast, the mechanical strength of PSNR-paper did not change, even after long time exposure to water. These results suggest the excellent nonwettability and enhanced integrity of PSNR-paper toward water infiltration even after printing. This is of great significance for the use of PSNR-paper in practical applications.

Endowing paper prints with superhydrophobicity is of great interest in real world applications. However, most conventional superhydrophobization methods cannot be used directly on paper-based prints. This is mainly because of the following: (i) the solvents used in a hydrophobization process would destroy the printed contents on paper surface due to dissolution of ink molecules; (ii) the opaque micro/nanotopographic features (i.e., surface roughness required for superhydrophobicity) reduce the readability/visibility of the printed content.

In this section, we demonstrate the feasibility of our strategy for waterproofing cellulosic papers preprinted with contents. Proof-of-concept experiments are shown in Figure 5. Interestingly, no observable change was inspected for the visibility and readability of the print (Figure 5a,b), which indicates the visible light transparency of the decorated PSNR layer. Further, the functionalized print appearance remains unchanged. However, the print treated with a conventional wet-chemical method showed unacceptable damage on both its exterior (curled surface) and the printed content (ink diffusion), caused by the used solvent during treatment (Figure S15).

The paper prints armored with PSNRs exhibit excellent waterproofing and self-cleaning functionalities; for example, muddy water jets bounce off easily from its surface without leaving any trace, whereas unmodified paper print was easily wetted and contaminated by the muddy water (Figure 5c,d and Movie S5). The static contact angle of a water droplet over PSNR-armored print surface was measured to be around 160°, and it remained unchanged after long-term exposure to water (Figure 5e). The $\theta_{CA}$ of the unmodified print was tested to be ~120°, and it instantly decreased to 0° after water exposure. The excellent waterproofing of the print armored with PSNRs can be attributed to the induced micro-nano surface morphology (Figure S16) as well as the low surface energy of PSNRs.[31]

The impact of PSNR armor on the print mechanical properties was investigated, as well, as shown in Figure 5e. Tensile measurements show that print armored with a PSNR layer features tensile strength comparable to that of the one without any modification, again confirming that the strategy employed does not affect the mechanical properties. The armored print exhibits significantly enhanced integrity and strength toward water exposure when compared with the untreated one, which is ascribed to its waterproof functionalization that prevented cellulose fibers from detaching due to water infiltration. The longevity of water repellency for the PSNR-armored print was evaluated under ambient conditions, as well. It was periodically examined through static contact angle measurements, and the $\theta_{CA}$ remains around 160° after 100 days of exposure (Figure 5f). Meanwhile, the self-cleaning properties were preserved as the dirt and dust contaminations can be easily removed from the print surface by rolling water droplets (Figure 5g). Notably, the decorated PSNR armor offers the functionalized paper items with excellent antimicrobial functionality. No microbial growth was observed over the PSNR-armored surface when it was exposed to the bacterial species under favorable growing conditions for 24 h (Figure 5h). On the contrary, bacterial colonies can be clearly observed on both the perimeter and surface of unmodified paper (Figure 5i), highlighting a large amount of microbial growth. The antimicrobial functionality can be attributed to the intrinsic superhydrophobicity of the PSNR-decorated surface, which prevents the microorganisms from accessing the moisture and nutrients that are required for growth. Moreover, the hierarchical structured surface resulting from the decorated PSNRs decreases the contact area between microbes and the solid substrate, which plays a vital role for reducing the adhesion of bacteria on the surface.[43] In addition, we also showed that the PSNR-armoring protocol can be applied to waterproof other cellulose-based products, such as packaging materials (Movie S6) and letter envelopes (Figure S17).

The above results have demonstrated the robustness of the engineered PSNRs for armoring cellulose-based items, i.e., endowing cellulosic objects with multifaced functionalities but without compromising their appearance and properties, which is promising for enhancing the usability of cellulosic items and providing great advantages in paper-based technologies.

## CONCLUSION

In summary, we have demonstrated a one-step strategy to fabricate printable superhydrophobic paper through in situ surface engineering with PSNRs. The PSNR-paper exhibits durable water repellency toward harsh external perturbations and shows significantly enhanced strength and integrity compared with traditional cellulosic paper after exposure to water. Importantly, the PSNR-paper features excellent printability toward widely used inkjet printing techniques and could sustain its water repellency after either printing or writing, due to the delicately designed oleophilic and hydrophobic PSNRs on its surface. Furthermore, the developed nonsolvent strategy can be directly applied on paper-based prints without compromising their readability and functionality, yet conventional wet-chemical methods cause irreversible damages to both the printed content and the cellulosic backbone. The PSNR provides the armored paper items with self-cleaning property and antimicrobial functionality, which could potentially mitigate aging and decomposition processes and extend the lifespan of paper-based items. This is of practical interest for the protection of paper-based items for outdoor use, as well as printed paper objects, such as historic papers, books, paintings, etc. Moreover, the PSNR armor strategy takes advantage of easy implementation, scalability, and the absence of organic solvents, which minimizes environmental and safety concerns and, in turn, provides opportunities for developing waterproof functional papers from sustainable natural resources.

## MATERIALS AND METHODS

**Materials.** Trichloroethylsilane (TCES, 98%) was purchased from ABCR GmbH (Germany). Cellulosic papers were purchased from Refutura (Germany). Toluene (99.8%), tetrahydrofuran (THF, ≥



https://doi.org/10.1021/acsnano.2c02382
ACS Nano 2022, 16, 9442−9451

99.5%), dimethylformamide (DMF, ≥ 99.8%), Rhodamine B (≥ 95%), hydrochloric acid (37%), and sodium hydroxide (≥ 97%) were purchased from Sigma-Aldrich. Ethanol and acetone (absolute for analysis) were purchased from Merck Millipore. Milli-Q water was produced by a Millipore Simplicity system (Billerica, MA, USA). Unless otherwise mentioned, all other chemicals were used as received.

**Sample Preparation.** To prepare the superhydrophobic paper engineered with polysilsesquioxane nanorods, the impact of reaction time, humidity, and TCES amount on PSNR morphology was investigated (Figures S1 and S18). In order to successfully grow PSNR on a cellulosic paper surface, we selected a humidity of 50%, reaction time of 2 h, and TCES usage of 800 $\mu$L for the reaction. Briefly, cellulosic paper with a size of 10 cm × 10 cm was placed into a custom-built glass desiccator (with a volume of 6 L) and equilibrated for 2 h under a controlled humidity of 50% ± 1%. The humidity inside the desiccator was monitored with a EE23 (E+E Elektronik, Austria) hygrometer and adjusted using a mixture of dry and humidified $N_2$. Subsequently, to initiate the growth of PSNRs on the paper surface, 800 $\mu$L of TCES was injected into the desiccator and the reaction was conducted at room temperature (~22 °C) for 2 h. The obtained PSNR-decorated paper was cleaned with a nitrogen gun and placed under ambient conditions for 4 h before any further characterizations. The pure PSNR was obtained through scraping the surface of PSNR-decorated glass slides. For this purpose, 8 pieces of glass slides (75 mm × 25 mm × 1 mm) were decorated with PSNRs, with the same reaction conditions as those used for preparation of PSNR-paper. To prepare the PSNR-decorated paper with A4 size, a glass desiccator of 12 L was used. Two milliliters of TCES was injected into the desiccator, and the reaction was conducted at a relative humidity of 50% ± 1% (room temperature) for 6 h. The same reaction conditions were employed to armor the paper prints with PSNRs. The printing performed on the PSNR-paper or cellulosic paper of A4 size was conducted exclusively with an inkjet printer (Expression Premium XP-6100 color inkjet printer with Claria Premium Ink).

**Characterizations.** A high-resolution SEM combined with EDX (Zeiss Supra 50 VP, German) was used to characterize the surface structures of the samples. The electron acceleration voltage was set to 10 keV. Prior to SEM-EDX analysis, all samples were sputter-coated with a 5 nm layer of platinum. The contact angle and sliding angle measurements were performed using a contact angle goniometer OCA15 plus (Dataphysics, Stuttgart, Germany). The water droplets used for waterproof measurements are all with a volume of 10 $\mu$L. FTIR spectra were obtained with a Bruker vertex 70 attenuated total reflection (ATR) FTIR spectrometer equipped with an ATR single reflection crystal (Bruker Optic GmbH, Germany). The spectra were collected in the range of 400 $cm^{-1}$ to 4000 $cm^{-1}$ (64 scans), and the background spectra were recorded against air. An RPR-200 model reactor (SNE Ultraviolet Co., USA) equipped with eight UV lamps (SNE Ultraviolet Co., USA) with an emission wavelength at 350 nm was used to assess the UV resistance of the tested samples.

**Durability Test.** The durability of water repellency for the PSNR-paper under exposure to external perturbations was evaluated by measuring the static contact angle of water droplets on the tested paper surface. We applied various external perturbations, such as exposure to UV illumination, extreme temperatures (−196 °C and 200 °C), ultrahigh humidity (90% RH), strong acidic and basic liquids, as well as various polar and nonpolar organic solvents, to evaluate the durability of the paper surface. After each solvent treatment, the paper samples were dried under vacuum at room temperature for 6 h, and static water contact angles were measured. To access the water repellency durability, the PSNR-armored paper prints were kept in an ambient environment for 100 days, and the wettability was periodically examined through static contact angle measurements. To evaluate the superhydrophobicity of the PSNR-paper toward mechanical abrasion, an AB5000 Washability Tester (TQC, Germany) was used. The friction partner (polyurethane sponge) was mounted on a reciprocating sled oscillated with a certain stroke speed. The stroke distance, speed, as well as the applied load were 30 cm, 10 cycles $min^{-1}$, and 50 g, respectively. The contact angles of the abraded samples were investigated as a function of abrasion cycles.

**Mechanical Performance Tests.** The tensile measurements were performed with an Instron 3345 universal testing device (US). A gap of 40 mm was used in the tensile measurements, and the typical sample (paper) dimensions were 100 mm × 10 mm. The applied testing rate was 1 mm $min^{-1}$. For average values of the maximum stress and strain, at least three specimens were measured.

**Antimicrobal Activity Test.** Antimicrobial activity test was performed using *Escherichia coli* BL21 strain. Bacteria were grown in LB (Luria-Bertani) medium at 37 °C overnight. This bacterial culture was diluted with LB to the optical density at $\lambda$ = 600 nm of 0.02 ($OD_{600}$ = 0.02). Presterilized superhydrophobic and control materials were immersed in the respective bacterial cell culture dilution for 50 s and subsequently rinsed with 100 $\mu$L of $ddH_2O$. All samples were placed in the middle of the LB agar plates and incubated overnight at 37 °C. Pictures were taken under Leitz Laborvert light microscope (Ernst Leitz Wetzlar GmbH, Germany) with 100× magnification.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.2c02382.

Time-dependent characterization of PSNR, reaction formulas for hydrolysis and polycondensation of TCES, photos of water droplets on PSNR-paper and cellulosic paper, time-resolved images of water droplets rolling off from the tilted PSNR-paper surface after chemical corrosion, SEM of the PSNR-paper after chemical corrosion, photos showing waterproof property of the mechanically abraded PSNR-paper, SEM and EDX of the PSNR-paper after abrasion, water jet bounces off A4 sized paper armored with PSNR and infiltrates the unmodified A4 paper, A4 sized cellulosic papers treated with a conventional wet-chemical method and the proposed nonsolvent strategy, cellulosic paper and PSNR-paper of A4 size printed with the same pattern, water resistance of the printed PSNR-paper and cellulosic paper, water droplets on the printed PSNR-paper surface, rapid absorption and complete wetting of the ink on PSNR-paper, SEM of PSNR-paper after handwriting and printing, the print treated with a conventional wet-chemical method, SEM of the paper-based print armored with PSNR, waterproof functionality of the letter envelope armored with PSNR and SEM of cellulosic paper functionalized under different reaction conditions (PDF)

Movie S1: A water jet bounces off the PSNR-paper surface (MP4)

Movie S2: Water droplets roll off from the PSNR-paper surface after solvent corrosion (MP4)

Movie S3: Water resistance of A4 size PSNR-paper and cellulosic paper (MP4)

Movie S4: Water repellency of printed PSNR-paper and cellulosic paper (MP4)

Movie S5: Water resistance of the paper print armored with and without PSNR (MP4)

Movie S6: Water repellency of the PSNR armed paper packaging box (MP4)

## AUTHOR INFORMATION

### Corresponding Author

**Stefan Seeger** − *Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland;* orcid.org/0000-0003-2892-7468; Email: sseeger@chem.uzh.ch



https://doi.org/10.1021/acsnano.2c02382
*ACS Nano* 2022, 16, 9442−9451

## Authors

**Shanqiu Liu** − *Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland*

**Kangwei Chen** − *Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland;* orcid.org/0000-0002-2977-2464

**Alma Salim** − *Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland*

**Jingguo Li** − *Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland*

**Davide Bottone** − *Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland;* orcid.org/0000-0002-6133-5088

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.2c02382


## Author Contributions

S.L. and K.C. contributed equally to this work. The manuscript was written through contributions of all authors, and all the authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the Center for Microscopy and Image Analysis (ZMB) of University of Zurich for giving the access to the microscopic facilities.

## REFERENCES


(1) Ras, R. H. A.; Tian, X.; Bayer, I. S. Superhydrophobic and Superoleophobic Nanostructured Cellulose and Cellulose Composites. *Handbook of Nanocellulose and Cellulose Nanocomposites*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2017; Vol. *1*, pp 731−760.

(2) Zhong, J.; Zhu, H.; Zhong, Q.; Dai, J.; Li, W.; Jang, S.-H.; Yao, Y.; Henderson, D.; Hu, Q.; Hu, L.; Zhou, J. Self-Powered Human-Interactive Transparent Nanopaper Systems. *ACS Nano* **2015**, *9*, 7399−7406.

(3) Li, C.; Boban, M.; Snyder, S. A.; Kobaku, S. P. R.; Kwon, G.; Mehta, G.; Tuteja, A. Paper-Based Surfaces with Extreme Wettabilities for Novel, Open-Channel Microfluidic Devices. *Adv. Funct. Mater.* **2016**, *26*, 6121−6131.

(4) Baidya, A.; Ganayee, M. A.; Jakka Ravindran, S.; Tam, K. C.; Das, S. K.; Ras, R. H. A.; Pradeep, T. Organic Solvent-Free Fabrication of Durable and Multifunctional Superhydrophobic Paper from Water-borne Fluorinated Cellulose Nanofiber Building Blocks. *ACS Nano* **2017**, *11*, 11091−11099.

(5) Chen, S.; Li, X.; Li, Y.; Sun, J. Intumescent Flame-Retardant and Self-Healing Superhydrophobic Coatings on Cotton Fabric. *ACS Nano* **2015**, *9*, 4070−4076.

(6) Wang, T.; Isimjan, T. T.; Chen, J.; Rohani, S. Transparent Nanostructured Coatings with UV-Shielding and Superhydrophobicity Properties. *Nanotechnology* **2011**, *22*, 265708.

(7) Wang, D.; Sun, Q.; Hokkanen, M. J.; Zhang, C.; Lin, F.-Y.; Liu, Q.; Zhu, S.-P.; Zhou, T.; Chang, Q.; He, B.; Zhou, Q.; Chen, L.; Wang, Z.; Ras, R. H. A.; Deng, X. Design of Robust Superhydrophobic Surfaces. *Nature* **2020**, *582*, 55−59.

(8) Qian, B.; Shen, Z. Fabrication of Superhydrophobic Surfaces by Dislocation-Selective Chemical Etching on Aluminum, Copper, and Zinc Substrates. *Langmuir* **2005**, *21*, 9007−9009.

(9) Cheng, Y.; Zhu, T.; Li, S.; Huang, J.; Mao, J.; Yang, H.; Gao, S.; Chen, Z.; Lai, Y. A Novel Strategy for Fabricating Robust Super-hydrophobic Fabrics by Environmentally-Friendly Enzyme Etching. *Chem. Eng. J.* **2019**, *355*, 290−298.

(10) Pakdel, A.; Bando, Y.; Golberg, D. Plasma-Assisted Interface Engineering of Boron Nitride Nanostructure Films. *ACS Nano* **2014**, *8*, 10631−10639.

(11) Li, B.; Zhang, J. Polysiloxane/Multiwalled Carbon Nanotubes Nanocomposites and Their Applications as Ultrastable, Healable and Superhydrophobic Coatings. *Carbon* **2015**, *93*, 648−658.

(12) Li, Z.; Cao, M.; Li, P.; Zhao, Y.; Bai, H.; Wu, Y.; Jiang, L. Surface-Embedding of Functional Micro-/Nanoparticles for Achieving Versatile Superhydrophobic Interfaces. *Matter* **2019**, *1*, 661−673.

(13) Peng, C.; Chen, Z.; Tiwari, M. K. All-organic Superhydrophobic Coatings with Mechanochemical Robustness and Liquid Impalement Resistance. *Nat. Mater.* **2018**, *17*, 355−360.

(14) Li, Z.; Milionis, A.; Zheng, Y.; Yee, M.; Codispoti, L.; Tan, F.; Poulikakos, D.; Yap, C. H. Superhydrophobic Hemostatic Nanofiber Composites for Fast Clotting and Minimal Adhesion. *Nat. Commun.* **2019**, *10*, 5562.

(15) Zhu, T.; Cheng, Y.; Huang, J.; Xiong, J.; Ge, M.; Mao, J.; Liu, Z.; Dong, X.; Chen, Z.; Lai, Y. A Transparent Superhydrophobic Coating with Mechanochemical Robustness for Anti-Icing, Photocatalysis and Self-cleaning. *Chem. Eng. J.* **2020**, *399*, 125746.

(16) Gauthier, A.; Symon, S.; Clanet, C.; Quéré, D. Water Impacting on Superhydrophobic Macrotextures. *Nat. Commun.* **2015**, *6*, 8001.

(17) Stamm, A. J. Thermal Degradation of Wood and Cellulose. *Ind. Eng. Chem.* **1956**, *48*, 413−417.

(18) Nyström, D.; Lindqvist, J.; Östmark, E.; Hult, A.; Malmström, E. Superhydrophobic Bio-Fibre Surfaces via Tailored Grafting Architecture. *Chem. Commun.* **2006**, *34*, 3594−3596.

(19) Chen, F.-F.; Dai, Z.-H.; Feng, Y.-N.; Xiong, Z.-C.; Zhu, Y.-J.; Yu, Y. Customized Cellulose Fiber Paper Enabled by an In Situ Growth of Ultralong Hydroxyapatite Nanowires. *ACS Nano* **2021**, *15*, 5355−5365.

(20) Ogihara, H.; Xie, J.; Okagaki, J.; Saji, T. Simple Method for Preparing Superhydrophobic Paper: Spray-Deposited Hydrophobic Silica Nanoparticle Coatings Exhibit High Water-Repellency and Transparency. *Langmuir* **2012**, *28*, 4605−4608.

(21) Zhang, Y.; Ren, T.; He, J. Inkjet Printing Enabled Controllable Paper Superhydrophobization and Its Applications. *ACS Appl. Mater. Interfaces* **2018**, *10*, 11343−11349.

(22) Yang, H.; Deng, Y. Preparation and Physical Properties of Superhydrophobic Papers. *J. Colloid Interface Sci.* **2008**, *325*, 588−593.

(23) Khanjani, P.; King, A. W. T.; Partl, G. J.; Johansson, L.-S.; Kostiainen, M. A.; Ras, R. H. A. Superhydrophobic Paper from Nanostructured Fluorinated Cellulose Esters. *ACS Appl. Mater. Interfaces* **2018**, *10*, 11280−11288.

(24) Zhang, J.; Seeger, S. Superoleophobic Coatings with Ultralow Sliding Angles Based on Silicone Nanofilaments. *Angew. Chem., Int. Ed.* **2011**, *50*, 6652−6656.

(25) Chen, F.-F.; Zhu, Y.-J.; Xiong, Z.-C.; Dong, L.-Y.; Chen, F.; Lu, B.-Q.; Yang, R.-L. Hydroxyapatite Nanowire-Based All-Weather Flexible Electrically Conductive Paper with Superhydrophobic and Flame-Retardant Properties. *ACS Appl. Mater. Interfaces* **2017**, *9*, 39534−39548.

(26) Wen, G.; Guo, Z. Nonflammable Superhydrophobic Paper with Biomimetic Layered Structure Exhibiting Boiling-Water Resistance and Repairable Properties for Emulsion Separation. *J. Mater. Chem. A* **2018**, *6*, 7042−7052.

(27) Li, Q.; Liu, H.; Zhang, S.; Zhang, D.; Liu, X.; He, Y.; Mi, L.; Zhang, J.; Liu, C.; Shen, C.; Guo, Z. Superhydrophobic Electrically Conductive Paper for Ultrasensitive Strain Sensor with Excellent Anticorrosion and Self-Cleaning Property. *ACS Appl. Mater. Interfaces* **2019**, *11*, 21904−21914.

(28) Cao, P.; Xu, K.; Varghese, J. O.; Heath, J. R. The Microscopic Structure of Adsorbed Water on Hydrophobic Surfaces under Ambient Conditions. *Nano Lett.* **2011**, *11*, 5581−5586.

(29) Stojanovic, A.; Olveira, S.; Fischer, M.; Seeger, S. Polysiloxane Nanotubes. *Chem. Mater.* **2013**, *25*, 2787−2792.

(30) Artus, G. R. J.; Olveira, S.; Patra, D.; Seeger, S. Directed In Situ Shaping of Complex Nano- and Microstructures during Chemical Synthesis. *Macromol. Rapid Commun.* **2017**, *38*, 1600558.

(31) Zhang, L.; Zhou, A. G.; Sun, B. R.; Chen, K. S.; Yu, H.-Z. Functional and Versatile Superhydrophobic Coatings via Stoichiometric Silanization. *Nat. Commun.* **2021**, *12*, 982.
(32) Liu, S.; Yin, S.; Duvigneau, J.; Vancso, G. J. Bubble Seeding Nanocavities: Multiple Polymer Foam Cell Nucleation by Polydimethylsiloxane-Grafted Designer Silica Nanoparticles. *ACS Nano* **2020**, *14*, 1623−1634.
(33) Kim, H.; Kim, H.-G.; Kim, S.; Kim, S. S. PDMS−Silica Composite Membranes with Silane Coupling for Propylene Separation. *J. Membr. Sci.* **2009**, *344*, 211−218.
(34) Zhang, J.; Zhu, C.; Lv, J.; Zhang, W.; Feng, J. Preparation of Colorful, Infrared-Reflective, and Superhydrophobic Polymer Films with Obvious Resistance to Dust Deposition. *ACS Appl. Mater. Interfaces* **2018**, *10*, 40219−40227.
(35) Gao, X.; Jiang, L. Water-Repellent Legs of Water Striders. *Nature* **2004**, *432*, 36.
(36) Checco, A.; Rahman, A.; Black, C. T. Robust Superhydrophobicity in Large-Area Nanostructured Surfaces Defined by Block-Copolymer Self Assembly. *Adv. Mater.* **2014**, *26*, 886−891.
(37) Artus, G. R. J.; Jung, S.; Zimmermann, J.; Gautschi, H.-P.; Marquardt, K.; Seeger, S. Silicone Nanofilaments and Their Application as Superhydrophobic Coatings. *Adv. Mater.* **2006**, *18*, 2758−2762.
(38) Liu, S.; Zhang, X.; Seeger, S. Solvent-Free Fabrication of Flexible and Robust Superhydrophobic Composite Films with Hierarchical Micro/Nanostructures and Durable Self-Cleaning Functionality. *ACS Appl. Mater. Interfaces* **2019**, *11*, 44691−44699.
(39) Chandra, D.; Yang, S. Capillary-Force-Induced Clustering of Micropillar Arrays: Is It Caused by Isolated Capillary Bridges or by the Lateral Capillary Meniscus Interaction Force? *Langmuir* **2009**, *25*, 10430−10434.
(40) Chandra, D.; Yang, S.; Soshinsky, A. A.; Gambogi, R. J. Biomimetic Ultrathin Whitening by Capillary-Force-Induced Random Clustering of Hydrogel Micropillar Arrays. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1698−1704.
(41) Zimmermann, J.; Reifler, F. A.; Fortunato, G.; Gerhardt, L.-C.; Seeger, S. A Simple, One-Step Approach to Durable and Robust Superhydrophobic Textiles. *Adv. Funct. Mater.* **2008**, *18*, 3662−3669.
(42) Ursula Meisser. *Picture Gallery UZH*; https://uzh.canto.global/v/DAM/album/T132S?viewIndex=1&display=fitView&column=image&id=sgmlqhgb2t0170bhvmpq9i5s13 (accessed 2022-05-17).
(43) Encinas, N.; Yang, C.-Y.; Geyer, F.; Kaltbeitzel, A.; Baumli, P.; Reinholz, J.; Mailänder, V.; Butt, H.-J.; Vollmer, D. Submicrometer-Sized Roughness Suppresses Bacteria Adhesion. *ACS Appl. Mater. Interfaces* **2020**, *12*, 21192−21200.


https://doi.org/10.1021/acsnano.2c02382
*ACS Nano* 2022, 16, 9442−9451