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Printable and Versatile Superhydrophobic Paper via Scalable Nonsolvent Armor Strategy

Shanqiu Liu, Kangwei Chen, Alma Salim, Jingguo Li, Davide Bottone and Stefan Seeger*
Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland.

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 (PSNR). Excellent superhydrophobicity is attained on the functionalized paper surface with water contact angle above 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 PSNR concurrently armors 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.

Key words: 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, microfluidics device, currency as well as use in construction and industrial processes.[1-3] Owing to the monosaccharides 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 the 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 don't negatively affect its innate properties, *i.e.*, printability, writability and mechanical performances.

Various surface-engineering techniques, such as photolithography,[7] chemical etching,[8,9] plasma treatment,[10] nanoparticulates deposition,[11-15] *etc.*, haven 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 non-printability 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 (contained fluoride or 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 application. 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 of superhydrophobic paper that simultaneously features printability is, despite of 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 (PSNR). 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 PSNR provides 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 PSNR not only enhances the paper strength and durability against exposure to water but also provides 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 PSNR 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 polysilsesquioxane nanorods (PSNR) 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 PSNR on paper surface is illustrated in Figure 1c. Under a certain humid ambience, 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 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 PSNR (Figure S1) agrees well with the elaborated PSNR growth mechanism. The reaction formulas for the hydrolysis and polycondensation of trichloroethylsilane are shown in Figure S2. Owning to the presence of hydroxyl groups on cellulose surface, the formed PSNR is 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]

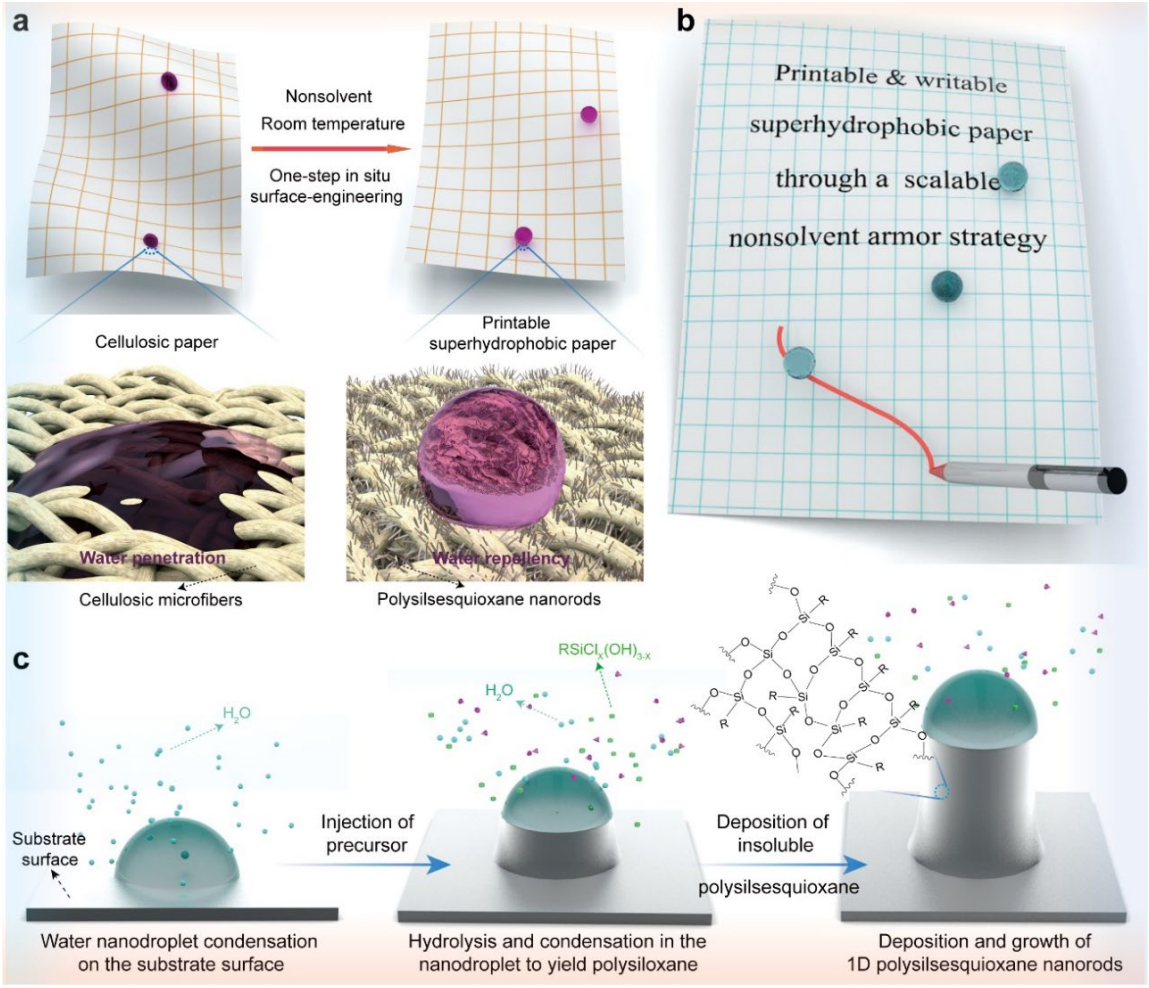

Figure 1. Illustration of the one-step nonsolvent strategy for designing printable superhydrophobic paper. Schematics showing (a-b) preparation of printable superhydrophobic paper *via in situ* surface-engineering of polysilsesquioxane nanorods (PSNR) and (c) growth mechanism of 1D PSNR.

After surface-engineering with PSNR, 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 uniformly decorated PSNR is further confirmed by the homogeneous distribution of 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 spectrums analysis for PSNR-paper (Figure 2g). In the 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 PSNR,[32,33] and same absorption bands are observed for pure PSNR (synthesis details are shown in experimental section) (Figure 2h). These results further prove the successful decoration of PSNR on paper surface. The PSNR layer thickness and the average diameter of PSNR were determined to be 7.0 ± 1.3 μm and 489 ± 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 grafting weight percentage of PSNR was calculated to be 19.8 ± 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 maintained non-wetting 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]

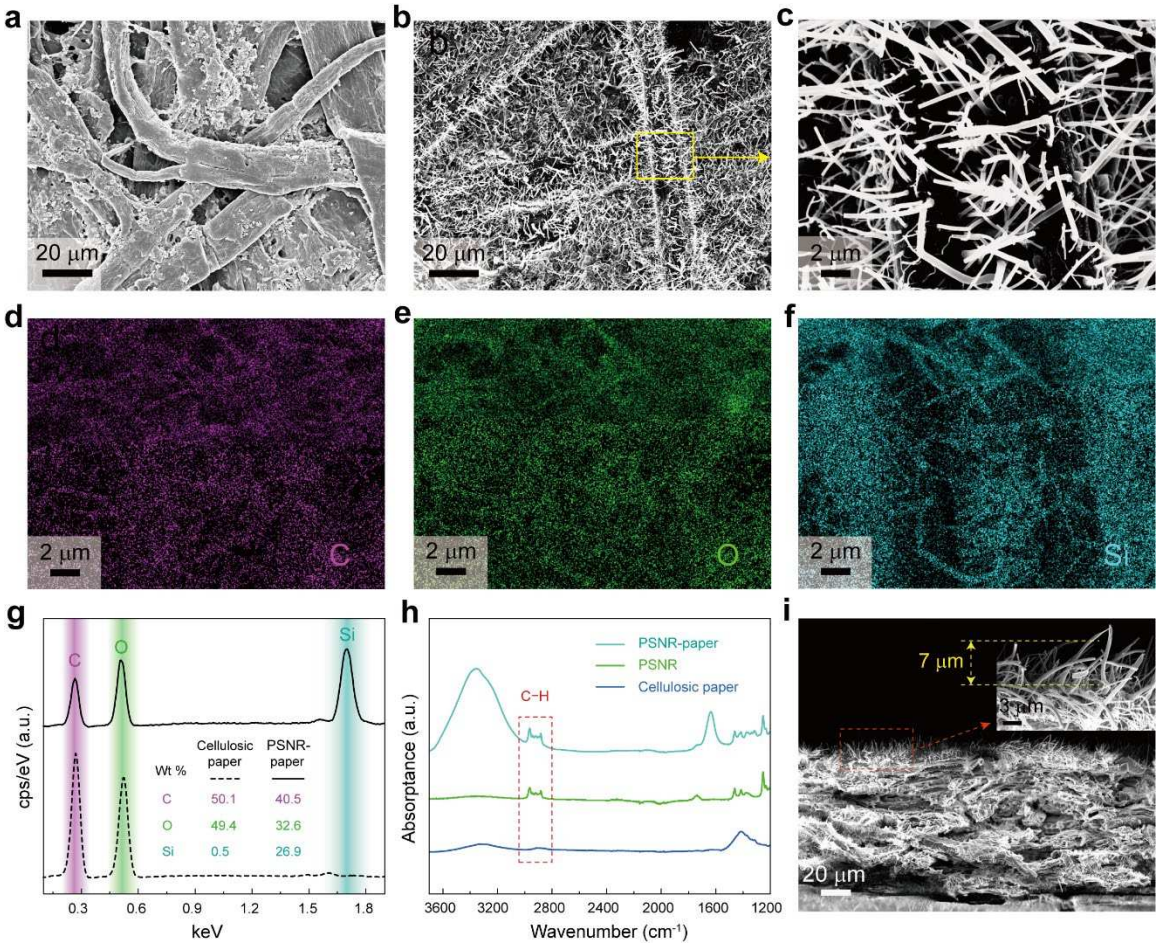

Figure 2. Structures and chemicals evaluation of PSNR-paper and cellulosic paper. Scanning electron microscopy (SEM) images of (a) cellulosic paper and (b-c) PSNR-paper at different magnifications, as well as (d-f) the corresponding energy-dispersive X-ray (EDX) mapping images. (g) EDX spectra of PSNR-paper 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.

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 (Θ_{CA}) measurements (Figure 3b). No obvious change in Θ_{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 Θ_{CA} above 150˚ (Figure 3c) despite of 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 Θ_{CA} of around 160 ˚C even after 24 hours 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 (5º) 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 provide excellent resistance towards 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 maintains intact with the paper surface after exposed to these corrosive liquids. The collapse of the PSNR after organic solvents treatment is ascribed to the induced capillary force during drying process.[39,40] The retained PSNR 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 Θ_{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 Θ_{CA} was observed despite 500 bending cycles. The preserved water repellency after mechanical damages can be ascribed to the maintained PSNR protected by the micro cellulose fibers during abrasion,[41] along with the residual polysilsesquioxane layer remained 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.

Notably, our strategy can be easily applied for scaleup 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 PSNR exhibits excellent water repellency 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 engineering with PSNR. 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.

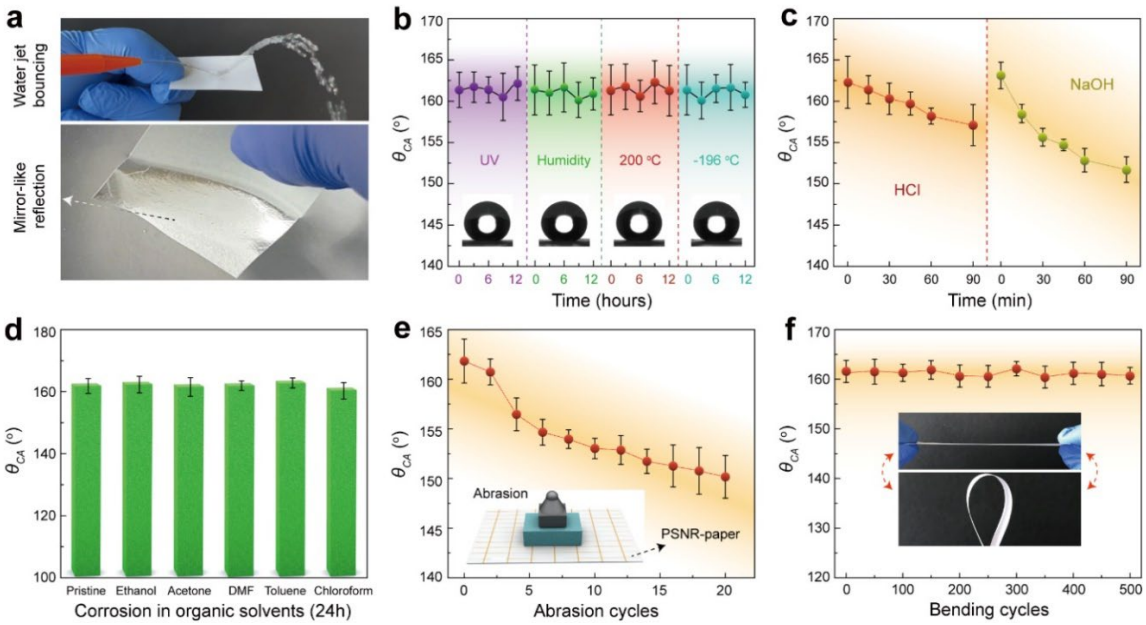

Figure 3. Ultradurable superhydrophobicity of the PSNR-paper: (a) A water jet bounces off PSNR-paper and the mirror-like plastron layer on the surface of PSNR-paper immersed in water. (b) Durability of PSNR-paper under exposure to UV illumination, high humidity (90% RH) and extreme temperatures (200 C˚ and -196 C˚). The inserted images showing the static contact angle of 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 (Θ_{CA}) of

PSNR-paper after 24 h corrosion from different tested organic solvents. Θ_{CA} as a function of (e) abrasion and (f) bending cycles. Inserts are the schemes of abrasion tests and images of bending tests.

Unlike superhydrophobic papers reported elsewhere, the as-prepared PSNR-paper can be used directly for printing, owning 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 outstanding printability of PSNR-paper. Importantly, the PSNR-paper even maintains its water repellency after been printed. A muddy water (10 g soil dispersed in 200 ml 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 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 with the printed cellulosic paper (Figure 4b, Figure S11b and Movie S4).

Moreover, the PSNR-paper enables handwriting as well. Figure 4c visually show 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 Rhodamine B dissolved with 10 ml ethanol) and exposed to water for a same time-period (12 h). The ink on 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 and e, respectively.

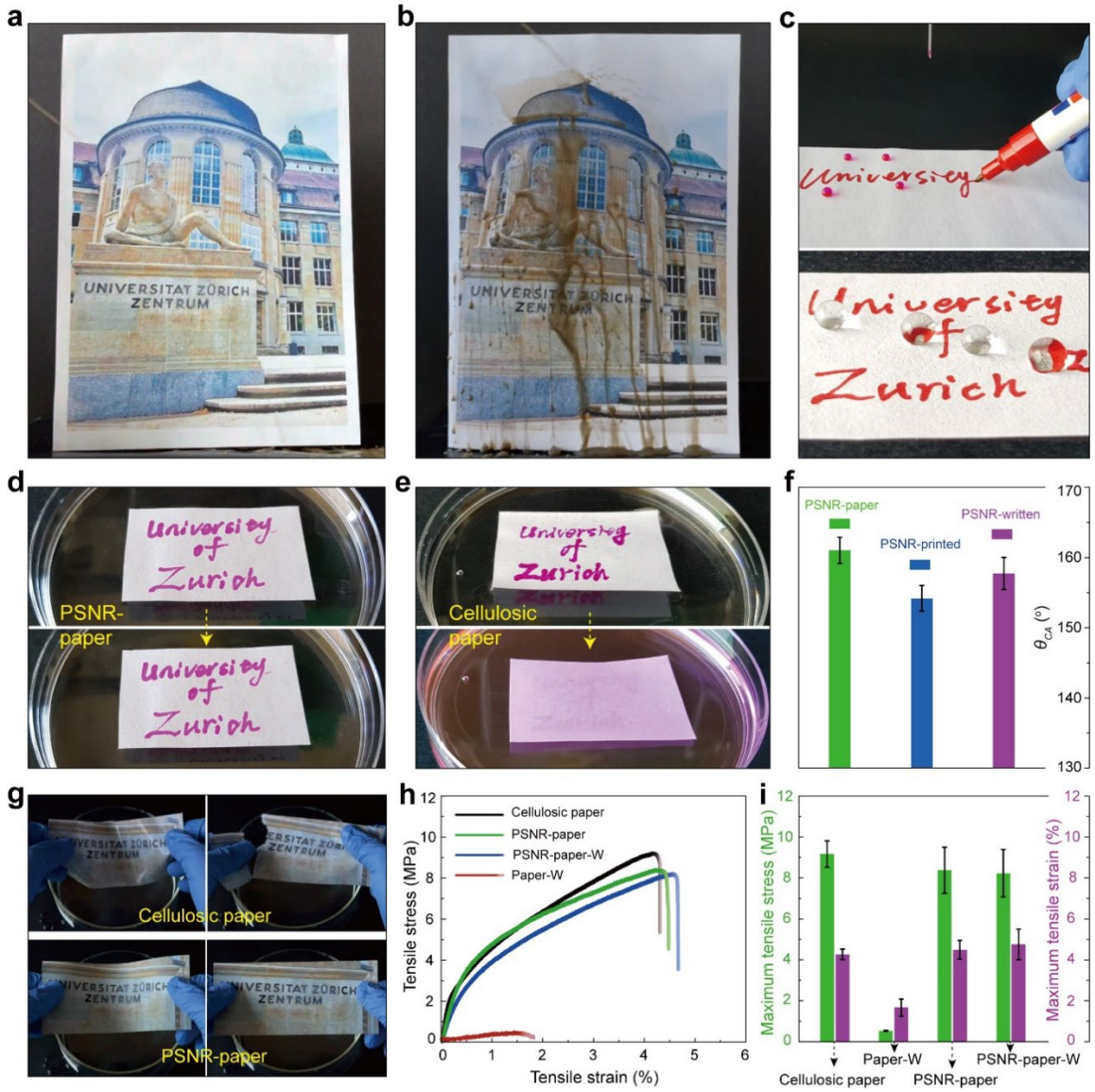

Figure 4. Printable and writable superhydrophobic paper with enhanced integrity. Comparison of water resistance between printed (a) PSNR-paper and (b) cellulosic paper. (c) Photos showing the hand writability of PSNR-paper and its preserved superhydrophobicity after handwriting. (d) Ink written on PSNR-paper remains intact on the surface after long term exposure to water, (e) while it diffuses easily from cellulosic paper to water. (f) Θ_{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.)

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 PSNR-paper surface. The oleophilicity of PSNR (attributed to the surface exposed ethyl groups) together with their micro-nano-rough structure result 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 0º) 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 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 property, tensile measurements were performed with the papers before and after water treatment (Figure 4h and 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 non-wettability 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.

On the other hand, endowing paper prints with superhydrophobicity is of great interest in real world applications, as well. However, most conventional superhydrophobization methods cannot be used directly on paper-based prints. This is mainly because: *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/nano topographic 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 pre-printed 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 damages on both its exterior (curled surface) and the printed content (ink diffusion), caused by the used solvent during treatment (Figure S15).

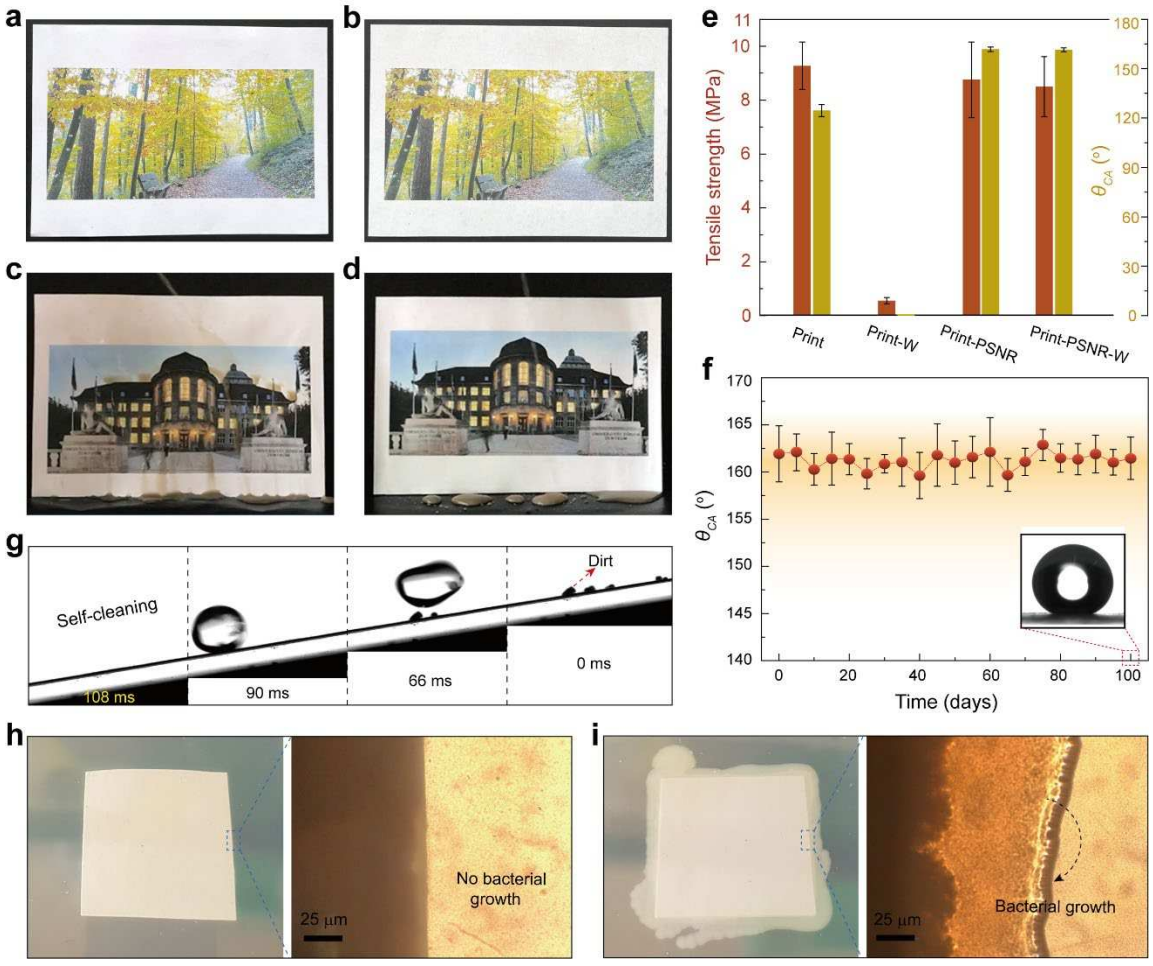

Figure 5. Transparent superhydrophobic armor for paper-based prints. Images showing paper prints (a) before and (b) after armoring with PSNR (print-PSNR). (c) The unmodified paper print contaminated by muddy water. (d) A jet of muddy water bounces off the print surface armored with PSNR. (e) Θ_{CA} and tensile strength for the prints (with and without

PSNR-armoring) before and after water exposure. Prints armored with and without PSNR 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 condition. The inserted photograph showing 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 condition. Comparison of antimicrobial property between (h) PSNR armored paper and (i) cellulosic paper. Photographs in Figures c and d are used with permission from University of Zurich. Copyright 2010 UZH Ursula Meisser.

The paper prints armored with PSNR exhibit excellent waterproofing and self-cleaning functionalities, *e.g.,* 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 Θ_{CA} of unmodified print was tested to be ~ 120˚ and it instantly decreased to 0˚ after water exposure. The excellent waterproofing of the print armored with PSNR can be attributed to the induced micro-nano surface morphology (Figure S16) as well as the low surface energy of PSNR.[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 PSNR layer features comparable tensile strength to the one without any modification, again confirming that the strategy employed does not affect the mechanical property. 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 PSNR armored print was evaluated under ambient conditions as well. It was periodically examined through static contact angle measurements and the Θ_{CA} remains around 160˚ after 100 days exposure (Figure 5f). Meanwhile, the self-cleaning properties was 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 PSNR decreases the contact area between microbes and solid substrate, which plays a vital role for reducing the adhesion of bacterial on the surface.[42] 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 PSNR for armoring cellulose-based items, *i.e.,* endowing cellulosic objects with multifaced functionalities but without compromise of 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 PSNR. 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 PSNR 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 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 METHOD

Materials. Trichloroethylsilane (TCES, 98%) was purchased from ABCR GmbH (Germany). Cellulosic papers were purchased from Refutura (Germany). Toluene (99.8%), tetrahydrofuran (THF, ≥ 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 (PSNR), the impact of reaction time, humidity and TCES amount on PSNR morphology were investigated (Figures S1 and S18). In order to successfully grow PSNR on cellulosic paper surface, we selected a humidity of 50%, reaction time of 2 h and TCES usage of 800 μL for the reaction. Briefly, cellulosic paper with 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 by using a mixture of dry and humidified N_2. Subsequently, to initiate the growth of PSNR on paper surface, 800 μL 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 (PSNR-paper) was cleaned with a nitrogen gun and placed under the ambient condition for 4 hours before any further characterizations. The pure PSNR was obtained through scraping the PSNR decorated glass slides surface. For this purpose, 8 pieces of glass slides (75 × 25 × 1 mm) were decorated with PSNR, 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. 2 ml 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 PSNR. 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 scanning electron microscope (SEM) combined with energy dispersive X-ray (EDX) (Zeiss Supra 50 VP, German) were used to characterize the surface structures of the samples. The electron acceleration voltage was set as 10 keV. Prior to SEM-EDX analysis, all the 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 μl. Fourier transform infrared (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 400-4000 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 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 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 50g, 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 λ=600 nm of 0.02 (OD_{600}=0.02). Pre-sterilized superhydrophobic and control materials were immersed in the respective bacterial cell cuture dilution for 50 sec, and subsequently rinsed with 100 μL 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 100x magnification.

ASSOCIATED CONTENT

Supporting Information

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

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

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

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

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

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

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.

AUTHOR INFORMATION

Corresponding Author

*Email: sseeger@chem.uzh.ch

Author Contributions

S. Liu and K. Chen 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 interests.

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