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Simple and Reliable Method to Incorporate the Janus Property onto Arbitrary Porous Substrates

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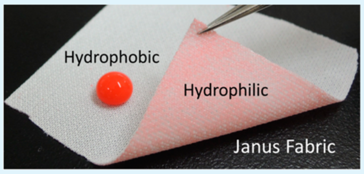
Supporting Information



ABSTRACT: Economical fabrication of waterproof/breathable substrates has many potential applications such as clothing or improved medical dressing. In this work, a facile and reproducible fabrication method was developed to render the Janus property to arbitrary porous substrates. First, a hydrophobic surface was obtained by depositing a fluoropolymer, poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate) (PHFDMA), on various porous substrates such as polyester fabric, nylon mesh, and filter paper. With a one-step vapor-phase deposition process, termed as initiated chemical vapor deposition (iCVD), a conformal coating of hydrophobic PHFDMA polymer film was achieved on both faces of the porous substrate. Since the hydrophobic perfluoroalkyl functionality is tethered on PHFDMA via hydrolyzable ester functionality, the hydrophobic functionality on PHFDMA was readily released by hydrolysis reaction. Here, by simply floating the PHFDMA-coated substrates on KOH(aq) solution, only the face of the PHFDMA-coated substrate in contact with the KOH(aq) solution became hydrophilic by the conversion of the fluoroalkyl ester group in the PHFDMA to hydrophilic carboxylic acid functionality. The hydrophilized face was able to easily absorb water, showing a contact angle of less than 37°. However, the top side of the PHFDMA-coated substrate was unaffected by the exposure to KOH(aq) solution and remained hydrophobic. Moreover, the carboxylated surface was further functionalized with aminated polystyrene beads. The porous Janus substrates fabricated using this method can be applied to various kinds of clothing such as pants and shirts, something that the lamination process for Gore-tex has not allowed.

KEYWORDS: *waterproof/breathable, hydrolysis, iCVD, Janus fabric, functionalization*

1. INTRODUCTION

Waterproof/breathable fabrics have attracted much attention for their wide applicability in the textile industry. The main purpose of the waterproof/breathable fabrics is to improve the ventilation of accumulated body fluids in the inner part of the clothing while protecting our body from the permeation of outer fluids such as rain and snow.[1] Such features can be achieved by having a water-repellent character from one surface, while perspiration and sebum can be readily absorbed and evaporated through the pores in the fabric to the other side.[2] While many methods[3−7] have been suggested to produce such fabrics, issues of high production cost and long-term mechanical robustness are still to be solved.[8−10] Gore-tex, a widely used and commercially available material, is made by the lamination of hydrophilic fabric with hydrophobic fabric,[11] but it is expensive and loses a significant degree of water repellency just by a few laundry cycles. Therefore, improving the mechanical stability is also of substantial importance for the long-term use of the waterproof/breathable fabrics. Therefore, the ideal way to achieve a cost-effective, highly efficient waterproof/breathable fabric is to introduce a Janus character directly to the desired fabric.

Here, we propose a simple method of rendering the two most important characteristics of Gore-tex—waterproof property and breathability—via an initiated chemical vapor deposition (iCVD) process using arbitrary porous substrates to fabricate porous Janus fabrics. The fabrication procedure involves depositing a hydrophobic polymer onto both sides of arbitrary porous substrates followed by a selective base-catalyzed hydrolysis to convert only one side of the hydrophobic porous substrate hydrophilic. The iCVD is highly advantageous to obtain such a fabric, in that it is possible to coat conformally on a wide range of desired substrate materials without damaging them.[12,13] Moreover, the iCVD process takes place at room temperature, which is attractive for various vulnerable substrates such as fabrics and papers that are prone to thermal damage.[14,15] On the other hand, solution-based coating methods can possibly damage the substrate due to the diffusion of functionalizing solutions into the bulk of the porous substrate arising from the capillary effect. Using these advantages of the iCVD process, Janus character was successfully rendered to various kinds of porous substrates such as polyester fabric, nylon mesh, and filter paper. The Janus substrates showed a high degree of hydrophobicity on one side and completely water-absorbing property on the other. As a result, the hydrophobic side showed no absorption of water, while the water absorption by the hydrophilic side reached 36.6% of the dry mass of the Janus fabric itself.

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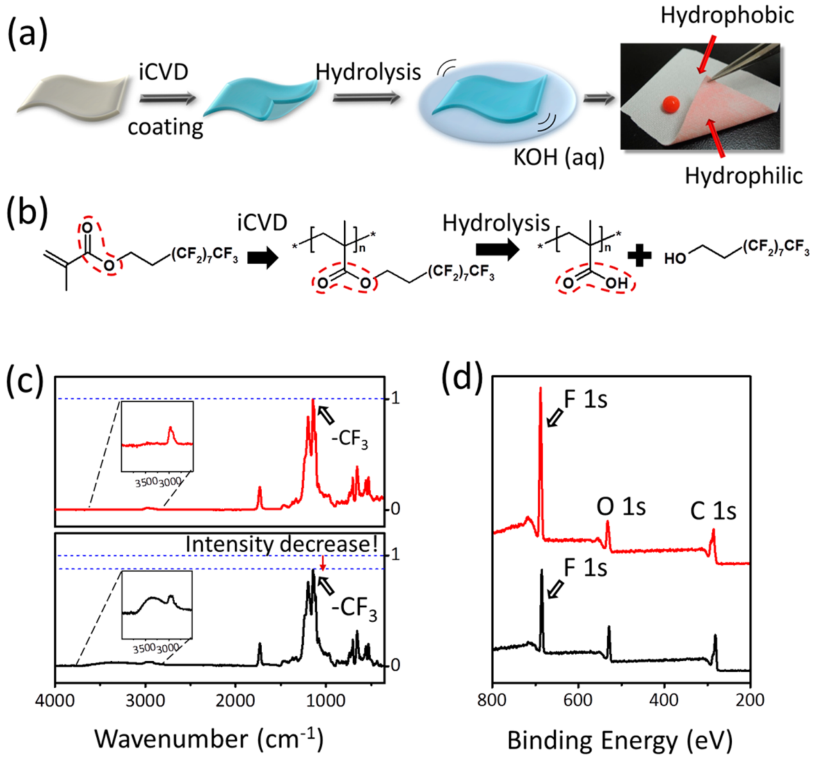

Figure 1. (a) Schematic procedure of the fabrication process of the porous Janus substrate: After coating the porous substrate conformally with PHFDMA using iCVD, the substrate was floated on top of KOH(aq) solution to hydrolyze the ester bond in the polymer and convert only one side of the PHFDMA-coated substrate to hydrophilic. (b) Reaction scheme for hydrolysis; after polymerization, the ester group (circled in red) is cleaved off by the KOH(aq) solution. (c) FTIR spectra of PHFDMA film before (top) and after (bottom) the hydrolysis. The decrease of peak intensity representing the $-CF_3$ functionality (shown as arrows) indicates the successful hydrolysis of PHFDMA. Newly emerged broad peak at 3300 cm^{-1} also shows the consequently formed −OH functionality (shown in the inset). (d) XPS survey scan spectra of PHFDMA-coated fabric before (top) and after (bottom) the hydrolysis. The decrease of peak intensity of F 1s (shown as arrows in d) was evident as the result of the hydrolysis reaction.

2. MATERIALS AND METHODS

2.1. Deposition of a Hydrophobic Polymer onto Porous Substrates via iCVD. To introduce the hydrophobicity, poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate) (PHFDMA) was deposited via initiated chemical vapor deposition (iCVD) process onto various porous substrates such as polyester fabric, nylon mesh, and filter paper. Both the monomer, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (HFDMA) (97%), and the initiator, *tert*-butyl peroxide (TBPO) (98%), were purchased from Sigma Aldrich and used without any further purification. Both HFDMA and TBPO were loaded into separate source cylinders, which were introduced to the iCVD reactor (Daeki Hi-Tech., Korea) at the flow rate of 1 standard cubic centimeter per minute (sccm) each. The thickness of the deposited film was determined by obtaining the cross-sectional scanning electron microscope (SEM) image (Nova 230, FEI) (see Figure S1 in Supporting Information (SI), for example). A 100 nm thin film of PHFDMA was conformally deposited onto the substrates with a rate of 17 nm/min. The reaction pressure, substrate temperature, and filament temperature were kept at 80 mTorr and 37 and 210 °C, respectively.

2.2. Introduction of Hydrophilicity to PHFDMA-Coated Substrates. The porous substrates coated with PHFDMA were exposed to a strong base solution to convert one side hydrophilic while not damaging the other. To achieve this, the coated substrates were floated on top of 1 M KOH(aq) solution to induce the cleavage of ester bond by the hydroxide ions in the KOH(aq) solution. The cleavage then resulted in carboxylic acids, which showed high hydrophilicity. However, the top face of PHFDMA-coated substrates that was not exposed to the solution still remained hydrophobic. The substrates were then rinsed with DI water to remove any adsorbed KOH(aq) solution.

2.3. Characterization. Fourier transform infrared spectroscopy (FTIR) of PHFDMA film before and after the hydrolysis was performed using ALPHA FTIR (Bruker Optics, USA) in normal transmission mode. A total of 64 scans were collected for each spectrum. X-ray photoelectron spectroscopy (XPS) survey scans were obtained using Sigma Probe Multipurpose XPS (Thermo VG Scientific, USA) with a monochromatized Kα source. Static water contact angles of the samples were measured using a Contact Angle Analyzer (Pheonix 150, SEO, Inc.) equipped with a microsyringe that can dispense 6 μL of water droplet. The optical microscope and fluorescence images were obtained from Eclipse 80i (Nikon, Inc.), equipped with a high-resolution digital camera (DS-Ri1, Nikon, Inc.).

2.4. Water Absorption Measurement. The amount of absorbed water from the hydrophobic side and hydrophilic side of the Janus fabric was measured by floating the fabric on a water bath kept at room temperature for a period of 10 s. After 10 s, the fabric was carefully removed from the surface of water and was patted with a dry cloth to remove excess water on top (ASTM D570).[16] For the case of the hydrophobic side, almost no water was absorbed since the low surface energy of the PHFDMA coating prevented the wetting. However, the hydrophilic side was wet immediately when floated and absorbed a significant amount of water.

2.5. Functionalization of Carboxylic Acid. The carboxylic acid groups resulting from hydrolysis were further functionalized with fluorescent amine-modified polystyrene beads (average diameter = 1 μm, Aldrich) using EDC−NHS conjugation chemistry.[17] For the functionalization, 10 mg of *N*-hydrosuccinimide (NHS) (98%, Aldrich) and 10 mg of *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) (98%, Aldrich) were dissolved in 100 g of deionized water (DI water). Then 200 μL of aqueous suspension of amine-modified polystyrene (PS) latex beads was prepared, and a piece of Janus nylon mesh was floated on the solution kept at 50 °C with stirring the solution with a magnetic bar. The beaker was completely covered with aluminum foil to minimize light penetration and thus the loss of fluorescence from the fluorescent PS beads. After running the reaction for 12 h, the fabric was removed, rinsed with DI water, and cleaned with ultrasonication for 5 min. The cleaning process removed all physically adsorbed latex beads, while the covalently bonded beads remained intact to the surface of the fabric.

3. RESULTS AND DISCUSSION

Figure 1a shows the schematic of the fabrication procedure of the Janus substrates. As an exemplary porous substrate, a piece of hydrophilic polyester fabric was conformally coated with a 100 nm thick hydrophobic polymer film, poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate) (PHFDMA) via iCVD. Polymers containing long fluoroalkyl chains such as PHFDMA are known to show a high degree of water repellency, with the water contact angle exceeding 150° on rough surfaces and extremely low contact angle hysteresis.[18] The iCVD process allowed for a conformal PHFDMA coating on both the top and bottom sides of the substrate with only a single iCVD coating step. The vapor-phase polymerization process allowed for the infiltration of vaporized initiators and monomers through the pores in the polyester fabric, as was observed previously.[19,20] The conformally coated PHFDMA film by iCVD was optically transparent. Our previous report indicated that the durability of the superhydrophobic surface in various harsh environments such as exposure to chemicals and heat was significantly improved and mechanically stable even after numerous laundry cycles. Moreover, it also sustained 20 000 times of abrasion test showing excellent stability against scratching.[21]

The hydrophobic, long perfluoroalkyl chain in the PHFDMA can be released simply by exposing one side of hydrophobic PHFDMA-coated fabric to a strong base in aqueous solution as shown in Figure 1b. The ester bond that links the fluoroalkyl chain to the polymer backbone was readily cleaved via base-catalyzed hydrolysis. As a result, the face exposed to the base solution was converted to be hydrophilic. To treat only one side of the porous substrate selectively, the hydrolysis reaction was performed simply by floating the nonwetting PHFDMA-coated polyester fabric on 1 M KOH(aq) solution. Then the face in contact with the solution lost its hydrophobicity and subsequently became hydrophilic.

Figure 1c shows the Fourier transform infrared (FTIR) spectra of the PHFDMA polymer before (top, in red) and after the hydrolysis (bottom, in black). All the peaks were normalized based on the intensity of the C═O peak, which is located at 1750 cm^{-1}, since the carbonyl peak remained unchanged even after the hydrolysis reaction. The intensity for the $-CF_3$ peak in the sample after the hydrolysis decreased slightly compared to that of the nonhydrolyzed sample (Figure 1c, arrows). Meanwhile, a peak indicating the formation of the hydroxyl group was observed at 3500 cm^{-1} which shows that the fluoroalkyl chain in the PHFDMA polymer was cleaved as a result of hydrolysis (Figure 1c, insets). The loss of perfluoroalkyl functionality by the hydrolysis was also distinctively detected in the X-ray photoelectron spectroscopy (XPS) survey scan spectra. As shown in Figure 1d, after the hydrolysis treatment, the intensity of the F 1s peak decreased significantly compared to its pristine film, indicating that the hydrolysis occurred successfully.

The floating method to introduce the hydrophilicity to hydrophobic, PHFDMA-coated substrate is highly advantageous in that the degree of hydrophilicity could easily be tuned by controlling parameters such exposure time, the hydrolysis temperature of KOH(aq) solution, and even the KOH concentration while not affecting the hydrophobic side. Figure 2a shows the relationship between the exposure time and the temperature of the KOH(aq) solution. As shown, the exposure time to KOH(aq) solution required to convert the hydrophobic surface to highly hydrophilic (water contact angle (WCA) ~ 30°) was found to be around 8 h at room temperature. However, when the temperature of the bath was increased to 75 °C, the time was reduced to around 10 min, showing an exponential decrease in the treatment time. On the other hand, the opposite top face without the contact with the KOH(aq) solution maintained its hydrophobicity even after 8 h of exposure at room temperature (Figure 2b). This can be attributed to the perfluoroalkyl groups in the polymer film that were unmodified to prevent the permeation of water into the bulk of the substrate. Thus, imparting the Janus property directly to porous substrates is particularly challenging compared to nonporous substrates. In the case of nonporous substrates such as slide glass, only one side can be selectively coated by various coating processes such as spin-coating or roll coating, simply because the nonporous substrate can effectively block the diffusion of the coating material to the other side of the substrate. However, it is difficult to coat only one side of a porous substrate selectively since the coating material can easily penetrate through the pores of the porous substrate. On the other hand, the iCVD process allows extremely conformal

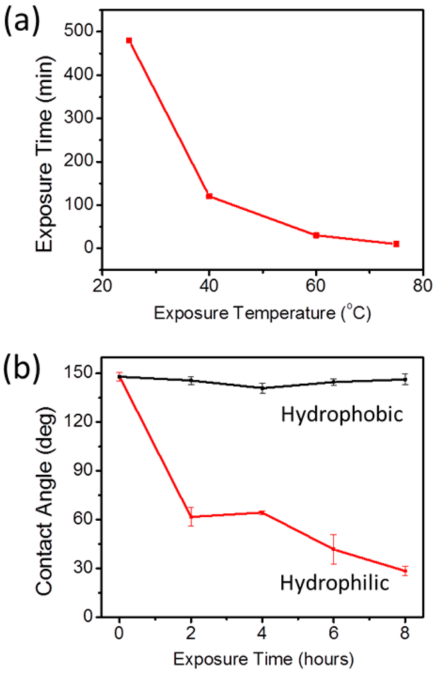

Figure 2. (a) Minimum required exposure time for polyester Janus fabric to reach water contact angle (WCA) < 30° is plotted as a function of temperature of 1 M KOH(aq) solution. As shown, as temperature increases, the time required for hydrolysis decreases exponentially. (b) Contact angle values of polyester Janus fabric exposed to 1 M KOH(aq) solution at 25 °C plotted as a function of exposure time. While the contact angle values on the face exposed to the solution (hydrophilic, red) decrease with increasing exposure time, the values for the unexposed face remain mostly the same (hydrophobic, black).

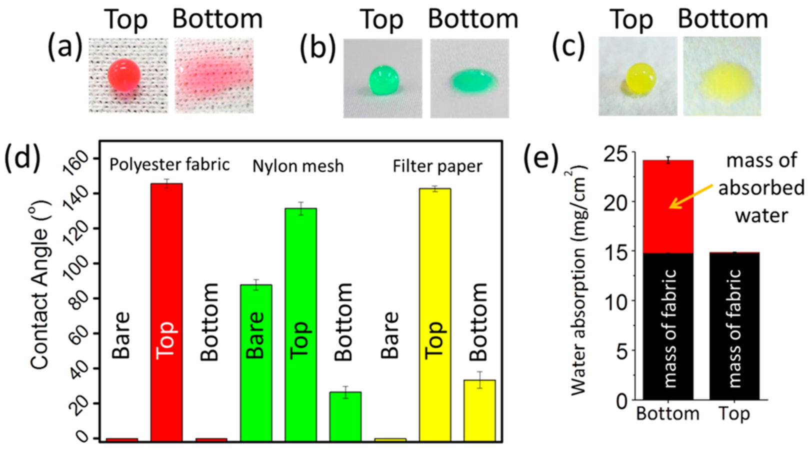

Figure 3. Images of water droplets on the Janus-faced surfaces with different substrates: (a) polyester fabric, (b) nylon mesh, (c) filter paper, respectively. The contact angle values of PHFDMA-coated substrate and the top side of the Janus substrate are very similar to each other, while that of the bottom side is significantly decreased. (d) The contact angle data for the bare substrate and top and bottom sides of the Janus substrate are also shown for the materials in a∼c. The water droplets in a∼c are dyed with aqueous red, green, and yellow inks, respectively. (e) Water absorption quantity of the hydrophilic side of the Janus fabric and hydrophobic side of the Janus fabric.

coating and preserves the surface morphology of the substrate. As a result, the pores of porous substrates remain undamaged as shown in Figure S2 in the SI. The SEM images in Figure S1 (SI) show that the size of the pores is on the order of tens to hundreds of nanometers, which remain preserved even after the deposition via iCVD. However, since the size of water molecules and air is on the order of a few Angstroms, the fabric can allow easy penetration of water molecules and air while efficiently blocking water droplets.

Therefore, the method presented here is advantageous in that (1) the conformal coating of porous substrates via iCVD allows for the use of various porous substrate materials and (2) the selective functionalization of only one side can be easily achieved from the interfacial reaction, simply by floating the fabric on the reactive solution while protecting the other side.

The nonlaminated, polyester Janus fabric obtained in this manner clearly displayed nonwetting, hydrophobic property on one face while possessing hydrophilic property on the other side (Movie S1 in SI). As shown in Movie S1 (SI), the hydrophilic face absorbed the aqueous ink solution immediately, while the hydrophobic face prevented any permeation of water even though the substrate was highly porous. In fact, water droplets even bounced back due to the high degree of hydrophobicity. This observation clearly demonstrates that the hydrophobic side was not damaged by the hydrolysis reaction.

Rendering Janus character was also successfully achieved in various kinds of porous substrates other than the polyester fabric. Materials such as nylon mesh and filter paper were also easily coated with PHFDMA via iCVD, and Janus property was directly incorporated to all these materials following the proposed method here (Figure 3). This was possible because the proposed method only utilizes the ester functionality in the iCVD PHFDMA, not the surface functionalities of the substrate materials themselves.[22] The surface characteristics of the porous substrate were completely masked by the conformal iCVD polymer coating, which enabled the material-independent, direct incorporation of Janus property to the porous substrates. Shown in Figure 3 are the images of various substrates coated with PHFDMA and those after the floating base-catalyzed hydrolysis, as suggested in Figure 1. The water contact angle of the hydrophobic side differs widely from that of the hydrophilic side arising from the generation of carboxylic acid groups. The contact angles were measured at the center and at the edges of a sample with at least 1 cm × 1 cm size to confirm that the hydrolysis did not damage the edges of the sample (see, for example, Figure S3 in SI). The contact angle of the hydrophobic side ranged from 132 to 157° depending on the degree of roughness of each substrate. Regardless of the substrate roughness, the water droplet was completely nonwetting on the hydrophobic side of the Janus fabric. The contact angle for the hydrophilic side was in the range of 0–37°, depending on the substrate materials and the base treatment conditions. No penetration of water droplet through the Janus fabric was observed. Notably, the contact angles of both hydrophobic and hydrophilic sides were highly dependent on the surface structure of the substrate, which affects the effective contact area between the water droplet and carboxylated substrate.[23]

For the Janus fabric to perform well for the outdoor clothing application, the hydrophilic side must absorb water readily, while the hydrophobic side repels water. For this purpose, the water absorption property of a Janus fabric produced from polyester fabric was investigated following the American Standard Test Method (ASTM) protocol.[16] Figure 3e shows the measure of the absorbed water by exposing the hydrophilic and hydrophobic face to water for 10 s. As shown in the figure, the absorbed amount of water to the hydrophilic surface of Janus fabric reached 36.6% of the dry mass of Janus fabric itself, while no detectable water absorption was observed from the hydrophobic side. The short exposure time of 10 s demonstrates that body fluids can be absorbed immediately while rejecting rain or snow from the outside. Therefore, the Janus fabric can be applied to areas where the lamination process for Gore-tex is not applicable such as dress pants or shirts.

The Janus fabric also displayed the Janus character when it was exposed to the mixture of water and different hydrophobic organic solvents such as chloroform. This was observed by placing the Janus fabric on top of water and chloroform (γ = 27.5 mN/m)[24] dyed with Oil Red O (Aldrich) and shaking it vigorously, as shown in Figure 4 and Movie S2 (SI). When the fabric was placed on top of water, facing the hydrophobic side

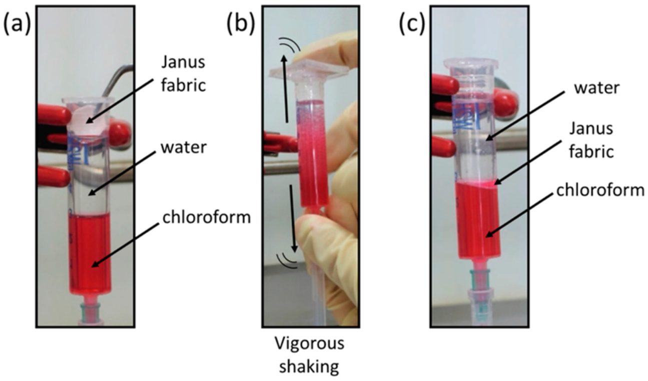

Figure 4. Still-shot images of polyester Janus fabric: (a) Janus fabric is placed on top of water and chloroform (dyed with Oil Red O). (b) The syringe is vigorously shaken to induce mixing. (c) Janus fabric is placed in the interface between water and chloroform (movie available as Movie S2 in the Supporting Information).

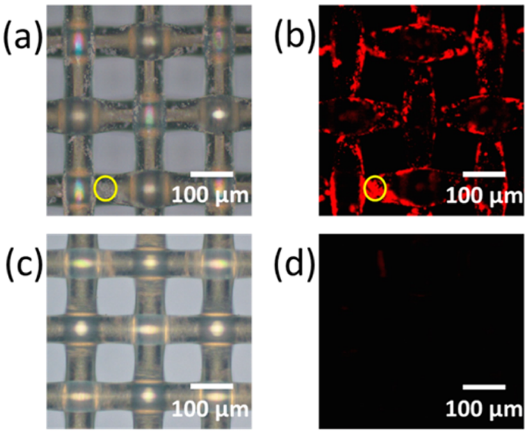

Figure 5. Functionalized Janus nylon mesh: (a), (b) optical microscope and fluorescence images of the hydrophilic side of Janus mesh functionalized with fluorescent PS particles, respectively. (c), (d) Optical microscope and fluorescence images of the hydrophobic side of Janus mesh, respectively (scale bar = 100 μm). The appearance of functionalized nylon mesh is similar to that of nonfunctionalized mesh except the presence of attached beads, indicated by a yellow circle, for instance.

to water to prevent the absorption of water to the Janus fabric, it floated on top of the water surface. However, when the mixture was vigorously shaken, the fabric placed itself at the interface of water and chloroform. This occurred because the hydrophilic surface of the Janus fabric preferred water and the hydrophobic surface with PHFDMA ($\gamma = 9.3$ mN/m)[25] favored the liquid with lower surface energy, chloroform in this case. Repeated vigorous shaking was applied for the effort to flip the fabric upside-down or to completely sink the fabric down to the bottom of the syringe, but the fabric was placed always at the interface between the water and chloroform, which clearly demonstrates the Janus characteristics of the fabric.

This result shows that: (1) the PHFDMA film coated by iCVD remains intact even after the exposure to organic solvents with additional mechanical stress and (2) the Janus fabric produced in this manner is applicable to various harsh environments. The fact that the fabric endures both chemical and mechanical stresses is a crucial factor for its application to outdoor clothing. It can also be applied in the manufacturing of daily clothing such as shirts or sweaters that requires waterproof/breathable properties.

Subsequent functionalization was also attempted after rendering the Janus property to the fabric. The hydrolyzed face could be functionalized further by conjugating various kinds of amine-containing materials with the carboxylic acids moiety from the hydrolysis. The functionalization was also easily achieved by floating the sample on top of a solution containing the amine-containing material, in the same manner as the hydrolysis step. Then, the carboxylic groups on the face in contact with the solution react with the amines, thus attaching the covalently grafted amine-modified material to the substrate simply via well-established carbodiimide chemistry with the *N*-hydroxysuccinimide (EDC–NHS) conjugation scheme.[17] This method is advantageous in that various surface properties could also be easily incorporated into the Janus fabric other than simple hydrophilicity.

As a proof of concept, a nylon Janus mesh was functionalized with amine-containing fluorescent-dye-tagged polystyrene (PS) (Aldrich) latex beads with a mean diameter of 1 μm. As shown in Figure 5, fluorescence was clearly observed from the hydrophilic side, while on the hydrophobic side, no apparent PS beads were detected. This is because the PS beads were covalently bonded to the carboxylic acid groups generated on the surface by hydrolysis via the EDC–NHS coupling. As a result of the strong covalent bonding, the beads remained intact to the substrate even after 5 min of ultrasonication treatment in water. In the optical microscope images, the appearance of both the functionalized and nonfunctionalized surfaces of the fabric was almost identical to each other except that the functionalized surface contains the attached beads, as marked by the yellow circle in Figure 5. Through the use of EDC–NHS coupling, it is possible to attach many other molecules such as proteins and DNAs with the primary amine group. Thus, by repeating the same procedure on the other side, the remaining hydrophobic side is also possible to be functionalized with other different functionalities. The thus formed dually functionalized fabric with arbitrary two functionalities can readily be formed by this simple method.

4. CONCLUSION

In conclusion, we demonstrated a simple and reliable method of rendering Janus character to various porous substrates such as polyester fabric, nylon mesh, and filter paper. The method presented in this work allowed the fabrication of Janus fabrics that can be applied as waterproof/breathable fabrics. Moreover, the proposed method is also applicable to a variety of other acrylate/methacrylate films with the hydrolyzable ester side chains, such as those containing epoxides, amines, furfuryl groups, and others.[26] Coupled with the functionalizability of carboxyl functionalities generated by the hydrolysis of acrylate/methacrylate iCVD polymers, a general methodology of endowing Janus character of two arbitrarily different surface properties on each side of the porous substrate is also anticipated by the use of the method proposed in this work.

Finally, the versatility and simpleness of the iCVD process allow a continuous roll-to-roll mode of operation as was demonstrated previously.[27] Therefore, the use of the iCVD process in fabricating porous Janus substrates can prompt their large-scale application to a variety of clothing such as pants and dress shirts, something that Gore-tex has not been able to achieve.

ASSOCIATED CONTENT

Supporting Information

Cross-sectional SEM image of Nylon coated via iCVD is shown in Figure S1. SEM images of before and after coating via iCVD are shown in Figure S2. Contact angle images and location where the contact angles were measured are presented in Figure S3. Movies S1 and S2 showing the performance of Janus fabric are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

‡Each author contributed in the preparation of this manuscript. All authors have given approval to the final version of the manuscript. J.B.Y. and Y.Y. contributed equally.

Notes

The authors declare no competing financial interest.

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