Highly Reliable Superhydrophobic Surface with Carbon Nanotubes Immobilized on a PDMS/Adhesive Multilayer

Kyung Kuk Jung, Young Jung, Chang Jun Choi, and Jong Soo Ko

ABSTRACT: We propose a new superhydrophobic surface that contains a carbon nanotube (CNT)-implanted poly(dimethylsiloxane) (PDMS)/adhesive multilayer. The adhesive provides very strong adhesion between the CNT-implanted PDMS layer and the substrate, and the CNTs on the surface exhibit superhydrophobicity. Therefore, the CNT-implanted PDMS/adhesive (CIPA) layer provides a highly reliable surface for superhydrophobicity. The fabricated CIPA surface performs far better than previously reported surfaces in terms of stability tests, such as contamination and solvent tests, and physical contact, including thermal pressure, bending, adhesion, and water jet tests. If a portion of the CIPA surface is destroyed, the surface is immediately restored because the material can regenerate the surface to its initial state. The surface can therefore maintain its superhydrophobicity even when damaged in rough environments, without self-healing or additional repair. Furthermore, because the adhesive is sprayed and coated on the surface of the substrate, a CIPA surface can be formed on three-dimensional shapes, including curved surfaces, and on various substrates.

1. INTRODUCTION

Because Neinhuis and Barthlott discovered the secret of the superhydrophobicity of the lotus leaf, the implementation of artificial superhydrophobic surfaces has been recognized as one of the most successful cases in biomimetics. In the past, researchers simply attempted to imitate the lotus leaf, whereas in recent years, artificial superhydrophobic surfaces have been applied to commercial products, such as solar cell panels, paints, and oil/water separation. A superhydrophobic surface is a surface that has a water contact angle of 150° or larger and a water sliding angle of 10° or smaller.

In general, two main technologies must be integrated to obtain an artificial superhydrophobic surface: nanoscale or microscale papillae should be formed on the surface of the substrate and a thin hydrophobic film must coat the entire surface, including the papillae. To date, the largest contact angle obtained from a hydrophobic solution coating without papillae on the surface is 120°. With the presence of nanoscale/microscale papillae, the contact area between a sample surface and water droplets decreases, reducing the surface energy. The papillae structure is therefore the core component in the fabrication of a superhydrophobic surface. However, because these nano-/micropapillae bulge on the surface, they can be easily damaged by physical contact.

Superhydrophobic surfaces have mostly been applied to surfaces for which physical contact is not significant, such as paint for structures and solar cell panels. Recently, however, they have been utilized in areas that do receive significant physical contact, such as paint for automobiles and clothes. It is thus important to be able to maintain superhydrophobicity by preventing damage caused by physical contact. When superhydrophobic surfaces are used on automobiles and clothing, they are likely to be exposed to frequent physical contact and strong hydraulic water pressure along with detergent during cleaning. Because of such unfavorable conditions, a highly reliable superhydrophobic surface structure that is physically robust and chemically stable must be developed to prevent the hydrophobic coating layer from peeling off and to keep the nano-/microstructures on the surface.

There have been many attempts to implement highly reliable superhydrophobic surfaces, including the use of hierarchical micro–nanostructures and repairable or self-healing surfaces. In the hierarchical method, if physical contact occurs, a microstructure that is a relatively large structure protects nanostructures, thereby maintaining superhydrophobicity. In the repairable fabrication method, a nanomaterial is sprayed onto the surface. This method can restore superhydrophobicity to the surface by spraying the nanomaterial on the defects.
caused by physical contact. Finally, in the self-healing method, when the surface is damaged, either hydrophobic components rapidly move to the destroyed area to restore the surface or the hydrophobic colloid spontaneously self-organizes to maintain superhydrophobicity.

In the hierarchical method, if the microstructure is broken or the surface is damaged by external contact, the surface loses superhydrophobicity. In the repairable method, because the damaged area must be reworked to restore the surface, the initially fabricated surface is not highly reliable. This method thus requires continuous reworking, and the surface may not be able to be restored if it is liquefied by chemicals such as solvents. The self-healing method also requires reworking the damaged area and therefore cannot produce a highly reliable initial surface either. Moreover, because it takes time to restore the damaged initial surface, the self-healing method cannot maintain a superhydrophobic surface well. This problem can be solved by manufacturing a durable superhydrophobic surface from the beginning so that it will not be damaged by physical or chemical contact. Many studies on manufacturing durable superhydrophobic surfaces have been performed. However, for the durable superhydrophobic structure, only poly(dimethylsiloxane) (PDMS) or plastic-type materials that already have hydrophobicity can be used. As a result, it cannot be applied to various surfaces. To overcome the aforementioned weaknesses of superhydrophobic surfaces, stronger and more reliable papillae can be fabricated that are robust to physical contact and not destroyed by solvents. To endure physical contact, the papillae must be very strong and strongly attached to the surface. Furthermore, the thin hydrophobic layer of the surface should not peel off easily.

Herein, we propose a new highly reliable superhydrophobic surface on which carbon nanotubes (CNTs) are strongly fixed on a PDMS/adhesive multilayer. Because of their strength and flexibility, CNTs are not easily damaged by physical contact and do not react with solvents. The strength of the adhesive between the substrate and CNT-implanted PDMS layer ensures that the attached layer cannot be easily detached from the surface of the substrate. Furthermore, because PDMS is hydrophobic and less reactive to organic solvents, it is suitable for maintaining a physically and chemically robust superhydrophobic surface. Because both CNTs and PDMS, the exposed materials, are hydrophobic, there is no need for additional hydrophobic coatings. When partial scratching and peeling of the top surface occur, a new water-repellent surface is revealed. This is consequently a suitable structure for maintaining superhydrophobicity. The physical stability of the prepared CNT-implanted PDMS/adhesive (CIPA) surface is evaluated by heat, pressure, hydraulic-pressure, and bending tests, and the chemical stability is evaluated by organic-solvent stability and cleaning ability tests. Tape tests reveal that the superhydrophobic CIPA surface is very robust to damage caused by adhesive materials. Finally, it is shown that the proposed CIPA surface can be applied to various substrates, such as metals, glasses, fibers, and polymers.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. The CIPA surface was composed of multiwall CNTs (MWCNTs, CM-250, Hanhwa Nanotech Corp., Korea), a Sylgard 184 PDMS prepolymer base (part A), a cross-linking curing agent (part B) (Dow Corning), and a spray adhesive (Super 99, 3M). The wet etching of PDMS was performed at room temperature under continuous stirring at a rotational speed of 500 rpm in a solution of N-methyl pyrrolidinone (NMP) (Alfa Aesar) and tetra-butyl ammonium fluoride (TBAF) (75 wt % in H₂O, Alfa Aesar). The ratio of NMP to TBAF/water was 3:1. To evaluate the stability of the organic solvents, acetone (99.98%, OCI Co., Korea), ethanol (99.98%, OCI Co., Korea), and isopropyl alcohol (IPA) (99.98%, OCI Co., Korea) were used. In addition, diesel (SK energy, Korea), vegetable oil (Beksul, Korea), and crude oil (SOKOL, SGS, Russia) were used to evaluate their stability to contamination. Doubly distilled and deionized (DI) water with a specific resistance over 18 MΩ-cm was used throughout the study.

A scanning electron microscope (SEM, S-4800, Hitachi, Japan) was used to analyze the surface morphology. The water contact angle was measured using a contact-angle meter (SEO, Korea), and the water sliding angle was measured using a tilting microscope (BXFM, Olympus, Japan). DI water was used to measure the contact and sliding angles. The size of droplet used in these measurements was 4 µL. Three specimens were
measured five times to determine the contact and sliding angles. We examined the physical properties of the CIPA surface by conducting heat, pressure, water jet, bending, and adhesion tests and examined the chemical properties by evaluating its stability to an organic solvent and contamination. For bending tests to determine sufficient flexibility, a CIPA layer was formed on the surface of cellulose-/polyester-based nonwoven fabrics (ww2109, KM, Korea). For other tests, a CIPA layer was formed on the surface of a copper sheet (99.9%, Kojundo, Japan).

2.2. Preparation of the CIPA Surface. Figure 1 shows the manufacturing process of the CIPA surface. First, a CNT-dispersed PDMS (CNT + PDMS) sheet was fabricated, as shown in Figure 1a. The PDMS precursor was prepared by mixing the PDMS prepolymer and the cross-linking agent at a ratio of 10:1 (w/w). CNTs of 5 wt % were then mixed with the PDMS precursor and degassed to remove air bubbles from the mixture under a vacuum condition \((5 \times 10^{-6} \text{ Torr})\) for 1 h. The CNT + PDMS mixture was filled in two plates 3 mm apart and was cured on a hot plate at 90 °C for 3 h. The surfaces of the fabricated CNT + PDMS sheet were etched in a PDMS wet etching solution at room temperature for 700 s and washed with DI water. Etching of the PDMS skin of the CNT + PDMS sheet exposed the CNTs, as shown in Figure 1a.

After the adhesive was thoroughly sprayed onto the surface of the substrate (Figure 1b), the PDMS sheet adhered to the surface of the substrate under 9.8 kPa pressure (Figure 1c). When a force was applied to detach the PDMS sheet from the substrate, a crack appeared on the side of the CNT + PDMS sheet (Figure 1d). After continuing to apply the force, the crack opened and the CNT + PDMS sheet was detached from the substrate (Figure 1e). As shown in Figure 1e, the CNTs were fixed to the PDMS and adhesive layers and some of the fixed parts of the CNTs were exposed outside of the PDMS surface. That is, the CIPA surface was covered with CNTs that were exposed outside of the PDMS surface.

2.3. Test Methods for Performance Evaluation of the Fabricated CIPA Surfaces. 2.3.1. Stability Test Against Heat and Pressure. To test the stability of the CIPA surface against heat, a CIPA-coated specimen was placed on top of a copper plate and heated from 50 to 300 °C in increments of 50 °C. The specimen was heated for 1 h using a hot plate (MSH-20D, Wised, Korea). To compare the thermal stability of the CIPA surface to that of a PDMS sheet, a pure PDMS sheet was manufactured and heated in the same way as the CIPA-coated specimen. After the heater was turned off, the specimens were left at room temperature for 60 min before their contact and sliding angles were measured. For the compression test, pressures of 0–10 000 kPa in 200 kPa increments were applied to the specimens. Compression was applied using a universal testing machine (ADMET) for 1 h. The contact and sliding angles of the specimens were measured 60 min after the compression had stopped.

2.3.2. Bending and Adhesion Tests. The bending test was performed by folding the specimen with two fingers in one direction and then folding it again in the opposite direction, which was defined as one cycle. In this test, the two sides folded inward were completely attached. Such bending creates very large tensile and compression stresses on the folded part of the CIPA surface. After 100 bending cycles, the contact angle was measured and surface damage was assessed using SEM. To test the adhesion of the CNTs to the CIPA layer and the bonding strength of the CIPA layer to the substrate, an adhesion test was conducted using scotch tape (Crystal Clear Tape, 3M). The tape was placed on the specimen, and then a force of 100 gf was applied for 10 min to the surface, after which the tape was peeled off. After repeating the tape bonding and peeling up to 20 times, the contact angle was measured, and the degree of detachment of the CNTs was assessed using SEM.

2.3.3. Water Jet Test. Water jet testing was conducted to examine the resistance of the CIPA surface to a high-pressure water spray. Water pressures ranging from 0 to 500 kPa were applied in 100 kPa increments. The nozzle and specimen were placed perpendicular to each other, 5 cm apart. The inner diameter and length of the nozzle were 5 and 10 mm, respectively. The water pressure was measured using a pressure sensor immediately before the pumped water escaped through the nozzle. The water jet was sprayed continuously for 10 min.
2.3. Stability Test for Organic Solvents and Contamination.

To evaluate the stability to organic solvents, three types of solvents were used: acetone, ethanol, and isopropyl alcohol. Prepared specimens were placed in each organic solvent for 6, 12, 18, and 24 h and then cleaned with water. The cleaned specimens were dried at room temperature for 12 h, and then their contact angles were measured. Additionally, three types of oil (i.e., diesel, vegetable oil, and crude oil) were utilized as contaminants to assess the stability of the specimens to contamination. A CIPA-coated specimen was contaminated by dropping 30 μL of oil on its surface and leaving the oil for 30 min. The contaminated surface was rinsed by flowing acetone across its surface for 1 min and then by flowing water for 60 s. The cleaned specimen was dried at room temperature for 12 h, and the contact angle of the contaminated area was measured.

3. RESULTS AND DISCUSSION

3.1. Surface Properties of the CIPA Layer. Figure 2 shows photos and SEM images of the CIPA-coated specimen. In Figure 2a, the black-colored surface is the CIPA-coated area. The CNT content of the CIPA surface shown in Figure 2 was 5 wt %, and the contact angle was larger than 160° on all of the manufactured surfaces. As shown in Figure 2b, when the specimen was put in water, the water was fully lifted off the surface by the CNTs, with air trapped between the CNTs. That is, a plastron formed on the surface of the fabricated specimen, and the surface of the submerged specimen was bright silver. When water droplets are fully lifted by CNTs, they follow the Cassie–Baxter wetting model and the contact angle can thus be calculated using the Cassie–Baxter equation: \( \cos \theta = -1 + f(\cos \theta_o + 1) \). Here, \( f \) is the solid fraction, which is defined as the ratio of the wetting area of the rough surface to the projected area, and \( \theta_o \) is the contact angle of a water drop on a smooth surface. \( \theta_o \) is determined by the chemical properties of the surface material, and \( f \) is determined by the morphology of the surface. Because CNTs are water-repellent and the contact area of a CNT with water is extremely small \( (f \ll 1) \), the CIPA surface must have a very large contact angle. Figure 2c shows a cross-sectional SEM image of the CIPA layer. The average thickness of the fabricated CIPA layer was 39 μm. Most of the CIPA layer consisted of CNT + PDMS layers, whereas the adhesive layer was very thin. Figure 2d,e show SEM images of the top of the CIPA surface. As shown in Figure 2d, the papillae of the CIPA surface have an irregular shape resembling a tangled vine. Figure 2e provides an enlarged SEM image of the top part of the papillae: densely entangled CNTs are exposed on the surface of the CNT + PDMS layer. The length of the exposed CNTs was measured to be 1.7 μm on average. The CNTs exposed on the CIPA-coated surface have the superhydrophobic property, and the PDMS layer under the CNTs is also water-repellent. Because water contacts only the CNTs, which have an extremely small diameter (100 nm), the solid fraction \( (f) \) is also extremely small, with the result that the CIPA surface becomes superhydrophobic. Even if water directly contacts the PDMS under very high pressure or when a water impact is applied, the water is instantly repelled from the surface because of the hydrophobic nature of the PDMS itself. Because of the hydrophobic nature of the two materials (CNT and PDMS) composing the surface, an additional coating of hydrophobic material is not necessary. Furthermore, damaged areas can be immediately restored with newly appearing CNT + PDMS surfaces.

The PDMS skin etching process, which is shown in Figure 1a, is very important for attaching a CNT + PDMS sheet to the substrate. When the adhesive was used without first etching the surface of the PDMS sheet, the PDMS sheet did not bond to the substrate. In contrast, when CNTs were exposed on the surface of the PDMS sheet, it easily bonded to the substrate with an adhesive (Figure 3d). The CNTs exposed by etching the PDMS skin are embedded into the spray-coated adhesive during the bonding process shown in Figure 1c. After curing the adhesive, the embedded CNTs grasp the solidified adhesive.
layer. Exposed CNTs therefore play a key role in bonding the CNT + PDMS layer to the substrate. In short, whereas CNTs exposed in the lower surface of the CNT + PDMS layer contribute to the strong bonding between the CNT + PDMS layer and the substrate, those exposed on the upper surface contribute to superhydrophobicity. The level of hydrophobicity of the CIPA surface depends on the CNT content. Figure 4 shows the changes in contact angle caused by varying the CNT content. At CNT contents of less than 1 wt %, few CNTs were transferred to the CIPA surface and, thus, the measured contact angle of the CIPA surface was similar to those measured from the surface of a pure PDMS sheet (∼115°). When the CNT content is 1.5–2.5 wt %, the contact angles rapidly increased; they increased more slowly above 2.5 wt %. All CIPA surfaces with the CNT content exceeding 2.5 wt % demonstrated superhydrophobicity.

Table 1 compares and summarizes various aspects of the physical and chemical performance of the proposed CIPA surface and existing superhydrophobic surfaces. While the CIPA surface performs similarly to those in other studies on the thermal test, it performs far better on tests of physical impact, such as pressure, bending, adhesion, and water jet, as well as on chemical tests using contaminants and organic solvents. The results and analysis of each test are described in detail below.

3.2. Stability for Heat and Pressure. Figure 5 presents the changes in the contact and sliding angles of the CIPA surface with respect to the temperature. For comparison, the change in the contact angle of a pure PDMS sheet according to temperature is also shown. For the CIPA surface, the contact angle was 163 ± 2° at the initial room temperature (20 °C) and changed to 157 ± 3° at 300 °C. Even when the temperature was elevated to 300 °C, the contact angle changed by only 6° compared to that at room temperature; that is, the CIPA surface successfully maintained its superhydrophobicity even at 300 °C. The sliding angle was maintained below 2° up for temperatures up to 200 °C and reached 3.7 ± 0.6° at 300 °C. This sliding angle is far smaller than the 10° required for a superhydrophobic surface.

The pure PDMS sheet exhibited a contact angle of 116 ± 2° at the initial temperature of 20 °C; at 250 °C, the angle changed to 113°, which is not a significant change. However, the angle rapidly decreased to 100 ± 6° at 300 °C. In contrast, the CNT can operate at very high temperatures, 1200 °C, and its material property does not change at 300 °C. In the temperature range of 250–300 °C, the change in contact angle of the CIPA surface was negligible but the change in

Table 1. Comparison of the Physical and Chemical Robustness of the Nanostructured Superhydrophobic Surfaces Reported to Date

| test parameter       | material (method)                                      | test limit | result at limit | reference  |
|----------------------|--------------------------------------------------------|------------|-----------------|------------|
| thermal stability    | MWCNT, PDMS (spray adhesive)                           | 300 °C     | 157 ± 3        | 3.7 ± 0.6  | this paper |
|                      | MWCNT, polysiloxane (spray coating)                    | 300 °C     | 0              | 1.3        | 35         |
|                      | candle soot, paraffin wax                              | 250 °C     | 156            | 6          | 36         |
|                      | PVDF, TiO<sub>2</sub> (coating)                        | 50 °C      | 155            | 8          | 38         |
|                      | MWCNT, formic acid, fluorosilane (spray coating)       | 400 °C     | 163            | 3          | 41         |
|                      | polystyrene, silica (coating)                          | 400 °C     | 135            | 50         | 11         |
| compression tolerance| MWCNT, PDMS (spray adhesive)                           | 10 000 kPa | 154 ± 4        | 2 ± 0.7    | this paper |
|                      | candle soot, paraffin wax                              | 500 kPa    | 162            | 1          | 36         |
|                      | polyethylene film, woven wire mesh (lamination)        | 550 kPa    | 160<sup>0.5</sup> | 5<sup>0.5</sup> | 34         |
|                      | PVDF, TiO<sub>2</sub> (coating)                        | 4000 kPa   | 152            |            | 38         |
|                      | PEI, PVDMA (coating)                                   | 6400 kPa   | 130            |            | 39         |
| water fall/jet        | MWCNT, PDMS (spray adhesive)                           | 500 kPa    | 158 ± 4        | 2 ± 0.4    | this paper |
|                      | MWCNT, polysiloxane (spray coating)                    | 30 kPa     | 160            | 18         | 35         |
|                      | candle soot, paraffin wax                              | 60 cm, 13 μL droplet | surface broken |            | 36         |
|                      | MWCNT, epoxy, resin (spray coating)                    | 45 kPa     | 163            |            | 37         |
| contamination         | MWCNT, PDMS (spray adhesive)                           | diesel (cleaning with detergent) | 161 ± 2 | 2 ± 0.5 | this paper |
|                      | zinc oxide, PDMS (coating)                             | dodecane (absorbed by porous structure) | 160 | 3 | 40 |
|                      | MWCNT, formic acid, fluorosilane (spray coating)       | hexadecane (repeat coating) | 166 | 3 | 41 |
| bending               | MWCNT, PDMS (spray adhesive)                           | folded with finger (180°, 100 cycles) | 160 ± 3 | 2 ± 0.5 | this paper |
|                      | PEI, PVDMA (coating)                                   | bending angle 10° | 163           |            | 39         |
| adhesion              | MWCNT, PDMS (spray adhesive)                           | scotch tape (stick and remove) | 158 ± 3 |            | this paper |
| solvent               | MWCNT, PDMS (spray adhesive)                           | acetone, ethanol, IPA (soak sample) | 160 ± 2 |            | this paper |

<sup>“Predicted value based on paper; blanks mean no values were measured.”</sup>
contact angle of the PDMS sheet was very large owing to the CNTs.42−44 If a droplet is simultaneously in contact with the CNTs and PDMS on the CIPA surface, the contact angle on the CIPA surface will substantially decrease because surface degradation of the PDMS occurs at 300 °C. Almost no change in contact angle on the CIPA surface was observed, which implies that the water droplets were fully lifted by the exposed CNTs on the CIPA surface. Therefore, even if the properties of the PDMS that fix the CNTs change, the CIPA surface can maintain superhydrophobicity.

Figure 5b illustrates the changes in the contact and sliding angles on the CIPA surface according to the applied pressure. When pressures of 0, 1000, and 10 000 kPa were applied to the surface, the measured contact angles were 164 ± 3, 158 ± 3, and 156 ± 4°, respectively. When the pressure was increased to 10 000 kPa, the contact angle decreased by 8°; thus, the CIPA surface successfully maintained its superhydrophobicity at a very high pressure. As the pressure was increased, the sliding angle increased gradually, indicating that the CIPA surface’s flatness increased with the pressure. Nevertheless, the sliding angle was only ∼2° at 10 000 kPa. Because the PDMS, which is an elastomer, and the CNT, which is 100 times as strong as steel, were bonded together, even under high pressure, the deformation was not large and the elastic resilience was excellent. When the pressure source was removed, because of the elasticity of the PDMS, the surface returned to its original structure and maintained its superhydrophobicity.

3.3. Bending and Adhesion. Figure 6 shows the results of the bending test. After 100 bending cycles, cracks had developed in the CIPA layer of folded region A−A′, as shown in Figure 6a. As shown in Figure 6b, the maximum crack width was 50 μm. Figure 6c shows an enlarged SEM image of...
the bottom of the crack. New CNTs that had been buried in the CNT + PDMS layer were exposed in the surface of the cracked area. On the PDMS sheet, a crack began to form when the sheet was bent back and forth, and the crack continued to the end until the sheet was completely broken. In contrast, on the CNT + PDMS layer, the crack did not reach the end of the sheet because of the binding force of the CNTs and their tangled morphology. Here, we observe that a new CNT-implanted PDMS surface was created across the entire surface, including both sides of the crack as well as the bottom of the crack. The new CIPA surface is manufactured by initiation of the crack and the separation of the CNT + PDMS layer, as shown in Figure 1d,e. The shape of the newly revealed cracked surface in the bending test is the same as that of the original CIPA surface. The measured contact angle on the cracked area was 160 ± 3°, which is similar to that measured on the CIPA surface without cracks (Figure 6d). The proposed CIPA surface therefore generates a new surface of the same structure as the original surface even if part of the surface has been physically destroyed. There is thus no significant change in the surface properties under bending.

Figure 7a shows a photo with two water droplets on the CIPA surface before the adhesion test (left) and after 20 cycles (right). The contact angle was 163 ± 2° before the adhesion test and decreased to 158 ± 3° after 20 cycles. As shown in the water droplet images in Figure 7a, the superhydrophobicity was maintained even after the test. SEM images of the adhesive side of the tape were recorded after each cycle to determine the shape and amount of material transferred to the tape’s surface during the adhesion test. Figure 7b contains SEM images of the adhesive side of the tape after one cycle. CNTs and pieces of PDMS from the CIPA surface were transferred to the tape’s surface, such that the shape of the tape’s surface resembled that of the CIPA surface. As shown in Figure 7c, as the number of cycles increased, the amount of material transferred from the CIPA surface to the tape’s surface was significantly reduced, until finally no transfer was observed on the 15th cycle. Immobilized CNTs on the CIPA surface with a bonding strength weaker than the adhesive strength of the tape were removed from the CIPA surface via tape attachment and detachment. This clearly shows that even after 20 cycles of the adhesion test the remaining CNTs on the CIPA surface were fixed onto the CIPA surface with a bonding strength greater than the adhesive strength of the tape.

3.4. Water Jet. Figure 8a shows the changes in the contact angle with increasing water pressure. The contact angle exceeded 160° for water pressure in the range 0–400 kPa and decreased to 158 ± 4° at 500 kPa. As shown in Table 1, the water pressure of 500 kPa is 11 times higher than the strongest water pressure (45 kPa) applied to nanosurfaces in previous studies. In the case of heavy rain, water pressure can be as high as 100 kPa; the CIPA surface can thus be used in an outdoor environment with heavy rain. When the water pressure was 400 kPa or less, the CIPA layer maintained its adhesion to the substrate. However, when the water pressure was above 500 kPa, the CIPA layer separated from the substrate, as shown in Figure 8b. The wrinkle-shaped delamination area was located at 3.3 mL away from the center of the water jet. As shown in Figure 8c, because of the strong water pressure spreading from the center of the water jet in a radial direction, a large shear stress (τ) was applied to the elastic PDMS. The accumulated shear stress in the CIPA layer increased with the distance from the center, and the separation began where the shear stress exceeded the critical fracture shear stress between the CIPA layer and the substrate. The shear stress inside the CIPA layer was released by the permanent deformation in the form of wrinkles rising above the separated CIPA layer. Figure 8d,e show top view SEM images of a specimen tested under a water pressure of 500 kPa. As shown in Figure 8e, some areas that were directly hit by the water jet were partially destroyed. This damage was observed only in the central part of the CIPA surface, which received a strong vertical water pressure from the water jet (region A of Figure 8c) but not in the regions where the water flowed in the lateral direction (region B of Figure 8c). The average contact angle measured in the area damaged by the water jet was 158 ± 4°, which is still an excellent value for superhydrophobicity. This is because, as analyzed in the previous bending test, new CNTs are exposed on the damaged surface and they regenerate surfaces similar to the initial CIPA surface, as shown in Figure 8e.

3.5. Stability to Organic Solvents and Oil Contamination. As shown in Table 2, even after the manufactured specimens were submerged in three organic solvents (acetone,
ethanol, and isopropyl alcohol) for 6, 12, 18, and 24 h, respectively, the changes in the contact angle were smaller than 3°. Furthermore, no interfacial peeling between the CIPA layer and the substrate was observed in any of the specimens. PDMS, which accounts for most of the CIPA layer, is very stable in organic solvents, and CNTs do not react with organic solvents.47,48 Because these two stable substances are bonded to the organic solvent, the initial superhydrophobicity can be maintained even if they are exposed to an organic solvent for a long time. As shown in Figure 9, the contact angles measured on surfaces contaminated by diesel, vegetable oil, and crude oil were 71 ± 4, 74 ± 3, and 83 ± 5°, respectively. After the contaminants were removed, the measured contact angles were changed to 161 ± 2, 159 ± 3, and 160 ± 3°, respectively, all of which are very similar to those measured before the contaminants were removed. On oil-contaminated surfaces, the chemical properties of the oil are the key determinants of the water repellency of the surface. After cleaning, the surface

Table 2. Change of Contact Angles of the CIPA Surfaces by Varying the Dipping Time in Three Different Organic Solvents

| test condition     | 6 h   | 12 h   | 18 h   | 24 h   |
|--------------------|-------|--------|--------|--------|
| acetone            | 162 ± 3° | 161 ± 3° | 163 ± 3° | 162 ± 3° |
| ethanol            | 160 ± 4° | 160 ± 2° | 160 ± 2° | 160 ± 2° |
| isopropyl alcohol  | 160 ± 2° | 162 ± 2° | 160 ± 3° | 161 ± 1° |

Figure 8. Water jet test results. (a) Change of contact angles according to the applied water pressure. (b) SEM image of protruded wrinkles formed at a water pressure of 500 kPa. (c) Schematic illustration of the mechanism of wrinkle formation. (d, e) SEM images of the CIPA surface after the water jet test with a water pressure of 500 kPa. The SEM images are of the center part of the CIPA surface (dotted area in (c)). The inner part of the dotted line shown in figure (e) was torn out by the strong water jet, thus forming a microsink.
almost recovered its initial chemical properties, regardless of
the type of pollutant. This proves that the CIPA surface is
chemically very stable for the surfactants used, i.e., oil-based
contaminants and cleaners. Generally, superhydrophobic
surfaces formed by conventional coatings are vulnerable to
chemicals such as organic solvents, oils, and surfactants and
thus the coated surface can be damaged.

As shown in Table 1, the proposed CIPA surface has far
better physical and chemical properties than those of other
superhydrophobic surfaces that have been developed to date.
Even if part of the surface is physically torn, a surface with
almost the same properties as those of the initial CIPA surface
is regenerated automatically and immediately. When the surface
is chemically polluted by oils, it can recover its initial state
with simple cleaning. The superhydrophobicity of the proposed
CIPA surface is therefore continuously maintained, even in
harsh physical and chemical environments.

3.6. Applicability of CIPA Coating on Various
Substrates. To confirm the possibility of CIPA layer
formation on various substrate materials other than copper
and nonwoven fabric, CIPA layers were formed on metal
(SUS304, iNexus, Inc., Korea), glass (Microscope Slides,
Duran, Germany), and plastic (polystyrene Petri dish, SPL,
Korea). The substrates were washed with ethanol (99.98%,
OCI Co., Ltd, Korea) and DI water and dried. The CIPA layer
formation process on these substrates is identical to that shown
in Figure 1. The CIPA surfaces formed on the four different
substrates are shown in Figure 10. All of the specimens
exhibited contact angles larger than 160°, and no CIPA layer
was separated from the substrate during the adhesion test using
adhesive tape. This result verifies that a CIPA surface can be
formed on various substrates that can be coated with an
adhesive and can also be formed on surfaces of three-
dimensional objects with curved surfaces.

4. CONCLUSIONS
We propose a new superhydrophobic surface that is sustainable
under physically and chemically harsh conditions. Whereas
some parts of the CNTs are fixed to the PDMS and an adhesive
multilayer bonded to a substrate, the remaining parts are
exposed on the outside of the surface. Both the CNTs and
PDMS exposed on the surface are hydrophobic, and the surface
is superhydrophobic because of the rough morphology of the
CNTs. The contact angles of the fabricated CIPA surfaces
exceeded 160°, and the sliding angles were below 2°. The CIPA
surfaces exhibit excellent superhydrophobic characteristics with
contact angles higher than 154° and sliding angles lower than
4° in all performance tests, including physical tests with heat,
pressure, bending, adhesion, and water jets and chemical tests
with organic solvents and surface contamination with oils.
These results are due to the excellent physical and chemical
properties of the CNTs and PDMS in the CIPA layer and the
immediate regeneration ability of a damaged CIPA surface. A
unique property of the CIPA surface is that the surface of a
damaged area is immediately restored to the initial CIPA
surface. Moreover, CIPA layers are easily formed on various
substrates, such as metal, glass, and plastic, and the contact
angle is higher than 160° on all of the CIPA surfaces. The

Figure 9. Stability test results of the CIPA surface for oil contamination: (a) diesel, (b) vegetable oil, and (c) crude oil. Whereas the photos on the
left show the contaminated states, those on the right show the repaired surfaces with the cleaning process. The liquid dropped on all surfaces is
water. The size scale is the same.
The proposed CIPA surface can thus be directly applied to superhydrophobic surfaces that may be exposed to harsh environments.

**AUTHOR INFORMATION**

*Corresponding Author*
E-mail: mems@pusan.ac.kr. Tel: +82-51-510-2488. Fax: +82-51-514-0685.

**ORCID**
Jong Soo Ko: 0000-0002-4707-7772

**Author Contributions**
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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