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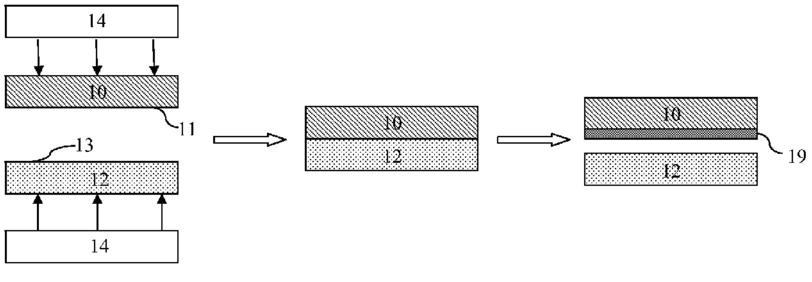

FIG. 1

(57) Abstract: The disclosure relates methods of preparing a superhydrophobic surface. The methods include laminating a polymer sheet having a surface to a template having a textured surface or a layer of a nanomaterial (e.g., nanoparticles or nanofibers) to convert the surface of the polymer sheet to a hydrophobic surface having a water contact angle of at least about 150°.

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Polymers Having Superhydrophobic Surface

CROSS-REFERENCE TO RELATED APPLICATIONS

Under 35 U.S.C. §119, this application claims priority to U.S. Provisional Patent Application Serial Number 61/447,508, filed February 28, 2011, U.S. Provisional Patent Application Serial Number 61/447,515, filed February 28, 2011, and U.S. Provisional Patent Application Serial Number 61/555,888, filed November 4, 2011. The entire contents of the parent applications are hereby incorporated by reference.

TECHNICAL FIELD

This disclosure relates to polymers having a superhydrophobic surface, as well as related methods and articles.

BACKGROUND

Superhydrophobic surfaces having a water contact angle greater than 150° and a water slip-off angle less than 10° can have many potential applications, such as from small non-wetting micro/nanoelectronics to large self-cleaning industrial equipment.

Numerous methods and materials have been developed to fabricate superhydrophobic surfaces. For practical applications, such surfaces should exhibit mechanical and chemical stability as well as abrasion resistance. For example, if a superhydrophobic surface is touched by a bare hand, the touched area of the surface could be contaminated by salt and oil and therefore could have an increased surface energy, which reduces the surface hydrophobicity. In addition, the force exerted by touching could damage the fragile rough structure of the surface, which could result in permanent loss of its superhydrophobicity. However, despite ongoing efforts, most reported artificial superhydrophobic surfaces suffer from poor mechanical and/or chemical stability.

In addition to mechanical and/or chemical stability, a commercially viable superhydrophobic surface should exhibit a reliable resistance to water pressure. In practice, a static pressure could be generated by immersing a hydrophobic surface under water and a dynamic pressure could be generated by applying water droplets or water streams onto a hydrophobic surface. Recent research shows that even a lotus leaf can be wetted within one hour after immersed under water at a depth of 0.55 m (i.e., under a water pressure of about 0.78 psi).

SUMMARY

This disclosure is based on the unexpected discovery that a polymer sheet having a superhydrophobic surface (e.g., having a water contact angle of at least about 150°) can be prepared in a facile method by laminating the polymer sheet with a template (e.g., a mesh) or a layer of a nanomaterial (e.g., nanoparticles or nanofibers). The superhydrophobic surface thus formed can have excellent mechanical properties, chemical resistance, abrasion resistance, and/or static and dynamic water pressure resistance. The method is a simple, low-cost process that is compatible with large scale manufacturing.

In one aspect, this disclosure features a method of preparing a hydrophobic surface that includes (1) laminating a polymer sheet having a surface to a template having a textured surface, the surface of the polymer facing the textured surface of the template; and (2) separating the polymer sheet and the template, thereby converting the surface of the polymer sheet to a hydrophobic surface having a water contact angle of at least about 150°.

In another aspect, this disclosure features a method of preparing a hydrophobic surface that includes laminating a polymer sheet having a surface to a layer of a nanomaterial, thereby converting the surface of the polymer sheet to a hydrophobic surface having a water contact angle of at least about 150°.

In still another aspect, this disclosure features an article that includes a polymer sheet having a hydrophobic surface, the hydrophobic surface having a water contact angle of at least about 150° and having a plurality of protrusions. The plurality of protrusions has an average length or width of from 2 μm to about 500 μm.

In still another aspect, this disclosure features an article that includes a polymer sheet having a hydrophobic surface and a plurality of nanoparticles disposed on the hydrophobic surface. The hydrophobic surface has a water contact angle of at least about 150°. At least some of the nanoparticles are partially embedded in the polymer sheet and partially exposed on the hydrophobic surface.

In still another aspect, this disclosure features an article that includes a polymer sheet having a hydrophobic surface, the hydrophobic surface having a water contact angle of at least about 150° after 1,000 abrasion cycles under a pressure of 32 KPa.

In yet another aspect, this disclosure features an article that includes a polymer sheet having a hydrophobic surface, the hydrophobic surface having a water contact angle of at least about 150° after the hydrophobic surface is scratched by a steel nail 10 times.

Embodiments can include one or more of the following features.

In some embodiments, the laminating step includes disposing the polymer sheet and the template between two plates. In such embodiments, the lamination step can further include pressing the two plates to bring the polymer sheet into contact with the template.

In some embodiments, the polymer sheet includes a polymer having a melting temperature and the laminating step is performed at a temperature above the melting temperature of the polymer. In such embodiments, the method can further include cooling the polymer sheet and the template below the melting temperature before separating the polymer sheet and the template.

In some embodiments, the laminating step is performed at a pressure of at least about 0.5 psi.

In some embodiments, the polymer sheet includes a thermoplastic or thermoset polymer. For example, the polymer can include a polyolefin, a polyacrylate, a poly(vinyl chloride), a polystyrene, a poly(tetrafluoroethylene), a polysiloxane, a polycarbonate, or an epoxy polymer. In some embodiments, the polymer can include a low density polyethylene, a high density polyethylene, a linear low density polyethylene, or an ultra-high molecular weight polyethylene.

In some embodiments, the polymer sheet can have a thickness of from about 25 µm to about 1 cm.

In some embodiments, the polymer sheet can further include an inorganic material (such as inorganic nanoparticles, inorganic microparticles, particle agglomerates, inorganic fibers, or inorganic nanofibers). In some embodiments, the polymer sheet can include a layer of inorganic nanoparticles on the surface. In such embodiments, the layer of inorganic nanoparticles can have a thickness of from at least about 1 μm, and can be porous.

In some embodiments, the template can include a mesh, a fabric, a porous membrane, or a sandpaper. For example, the template can include a mesh having an average pore size of from about 2 μm to about 800 μm. In such embodiments, the mesh can have an average depth of pores ranging from about 2 μm to about 800 μm.

In some embodiments, the method can further include disposing inorganic nanoparticles onto the template before the laminating step. In such embodiments, the inorganic nanoparticles can include SiO_2 nanoparticles, TiO_2 nanoparticles, Al_2O_3 nanoparticles, or carbon nanoparticles. In some embodiments, the inorganic nanoparticles can have an average diameter of from about 3 nm to about 1000 nm.

In some embodiments, the hydrophobic surface can have a water slip-off angle of at most about 5°.

In some embodiments, the hydrophobic surface can remain dry under a static water pressure of at least about 8 psi for at least about 5 hours.

In some embodiments, the laminating step can be performed by plate lamination, autoclave lamination, or roll lamination.

In some embodiments, the layer of the nanomaterial can be disposed on a template. In some embodiments, the layer of the nanomaterial can include inorganic nanoparticles (such as SiO_2 nanoparticles, TiO_2 nanoparticles, Al_2O_3 nanoparticles, or carbon nanoparticles). In such embodiments, the inorganic nanoparticles can have an average diameter of from about 3 nm to about 1000 nm.

In some embodiments, the hydrophobic surface can have a water contact angle of at least about 150° after 1,000 abrasion cycles under a pressure of 32 KPa.

In some embodiments, the hydrophobic surface can have a water contact angle of at least about 150° after the hydrophobic surface is scratched by a steel nail 10 times.

In some embodiments, the plurality of protrusions can have an average height of from about 25 μm to about 1000 μm.

In some embodiments, the plurality of protrusions can have an average distance of from about 5 μm to about 500 μm between two neighboring protrusions.

In some embodiments, the polymer sheet can include a plurality of protrusions on the hydrophobic surface, each protrusion having a top surface and a side wall. In such embodiments, at least some of the nanoparticles are disposed on the top surface and the side wall of each protrusion. In some embodiments, the polymer sheet can have a surface between two neighboring protrusions and at least some of the nanoparticles are disposed on the surface between two neighboring protrusions. In such embodiments, the surface between two neighboring protrusions and the top surface of a protrusion have an average distance of from about 2 μm to about 800 μm.

In some embodiments, the polymer sheet can include a plurality of protrusions on the hydrophobic surface, the protrusions having an average length or width of from 0.5 μm to about 10 μm.

Other features, objects, and advantages will be apparent from the description, drawings, and claims.

DESCRIPTION OF DRAWINGS

FIG. 1 is an illustration showing an exemplary method of using plate lamination for preparing a polymer sheet having a superhydrophobic surface by laminating the polymer sheet with a template.

FIG. 2 is an illustration showing an exemplary method of using plate lamination for preparing a polymer sheet having a superhydrophobic surface by laminating the polymer sheet with a layer of a nanomaterial (e.g., nanoparticles or nanofibers).

FIG. 3(a) is an illustration showing another exemplary method of using roll lamination for preparing a polymer sheet having a superhydrophobic surface by laminating the polymer sheet with a layer of nanoparticles or nanofibers. FIG. 3(b) is an illustration showing another exemplary method of roll lamination.

FIG. 4 is an illustration showing another exemplary method of using plate lamination for preparing a polymer sheet having a superhydrophobic surface by laminating the polymer sheet with a template coated a layer of a nanomaterial (e.g., nanoparticles or nanofibers).

FIG. 5 is an illustration of an exemplary polymer sheet having a superhydrophobic surface.

FIG. 6 is an illustration of another exemplary polymer sheet having a superhydrophobic surface.

FIGs. 7(a)-7(f) are SEM images of surfaces fabricated in Example 1 by using mesh 1 (M1) at different temperatures under the same pressure: (a,b) surface S1, 115 °C. (c,d) surface S2, 120 °C, and (e,f) surface S3, 125 °C. Panels b, d, and f are higher magnification views of panels a, c, and e, respectively.

FIGs. 8(a)-8(f) are SEM images of surfaces fabricated in Example 1 by using different mesh templates at the same lamination temperature and pressure: (a,b) surface S4 made from mesh 2 (M2), (c,d) surface S5 made from mesh 3 (M3), and (e,f) surface S6 made from mesh 4 (M4). Panels b, d, and f are the higher magnifications of panels a, c, and e, respectively.

FIGs. 9(a)-9(d) are images of surface S6 in Example 1 after manual abrasion testing: (a) being an image of S6 touched with a bare finger, (b) being an image of water droplets on a partly dried surface S6 after a multi-step manual test, (c) being an image of water contact angle of surface S6 after the same multi-step manual test, in which the surface was rinsed with water and dried before measuring, and (d) being a SEM image of the surface structure of S6 after the same multi-step manual test, in which the surface was rinsed, dried and coated with gold before imaging.

FIG. 10(a) is a graph showing that the water contact angle of superhydrophobic surface S4 in Example 1 as a function of abrasion cycles using the Taber reciprocating abraser under a pressure of 32.0 kPa. FIG. 10(b) is an image of water droplets on surface S4 after 2000 cycles of mechanical abrasion testing. The abrasion region lies between the two parallel dashed lines.

FIGs. 11(a)-11(h) are SEM images of Samples 1-3 in Example 2 after different treatments using UHMWPE as polymer substrate: (a, b) being the SEM images of an original UHMWPE substrate in Sample 1, (c, d) being the SEM images of the UHMWPE substrate in Sample 2 after heating to 154°C and cooling to 25°C (but without coating with a layer of nanoparticles), (e, f) being the SEM images of the UHMWPE substrate in Sample 3 (which was coated with a layer of nanoparticles) after heating to 154°C and cooling to room temperature 25°C, and being before etched with a 49% HF acid for 8 hours, and (g, h) being SEM images of the UHMWPE substrate in Sample 3 after being etched with a 49% HF acid for 8 hours.

Panels b, d, f, and h are higher-magnification views of panels a, c, e, and g, respectively.

FIGs. 12(a)-12(d) are SEM images of Sample 4 in Example 2 in which a polymer sheet and a layer of nanoparticles were laminated under a pressure of 83 psi: before (a) and after (b, c, and d) being etched with a 49% HF acid. Panel c is a higher-magnification view of panel b and panel d is the higher-magnification view of panel c.

FIGs. 13(a)-13(d) are the SEM images of Sample 8 in Example 2 in which a polymer sheet and a layer of nanoparticles were laminated under a pressure of 8000 psi: before (a) and after (b, c, d) being etched with a 49% HF acid. Panel c is the higher-magnification view of panel b and panel d is the higher-magnification view of panel c

Like reference symbols in the various drawings indicate like elements.

DETAILED DESCRIPTION

This disclosure generally relates to polymers having a superhydrophobic surface (e.g., having a water contact angle of at least about 150°), as well as methods of preparing such polymers.

In general, the methods disclosed herein include laminating a polymer sheet having a surface to a template having a textured surface or a layer of a nanomaterial (e.g., nanoparticles or nanofibers) to convert the surface of the polymer sheet to a hydrophobic surface having a water contact angle of at least about 150°.

The polymer sheet described herein can include either a thermoplastic polymer or a thermoset polymer (or its precursors). In some embodiments, the polymer sheet described herein preferably includes a thermoplastic polymer. Exemplary of suitable polymers that can be used in the polymer sheet include polyolefins (e.g., polyethylenes or polypropylenes), polyacrylates (e.g., poly(methyl methacrylate)s), poly(vinyl chloride)s, polystyrenes, poly(tetrafluoroethylene)s, polysiloxanes, polycarbonates, or epoxy polymers. Examples of suitable polyethylenes include low density polyethylenes, high density polyethylenes, linear low density polyethylenes, and ultra-high molecular weight polyethylenes. In some embodiments, the polymer sheet described herein can be made of two or more (e.g., three, four, or five) different polymers, such as two or more different polymers described above. In some embodiments, a liquid polymer (e.g., a polysiloxane) can be combined with at least one inorganic material (e.g., inorganic particles, inorganic microparticles, inorganic nanoparticles, particle agglomerates, inorganic fibers (e.g., glass fibers), or inorganic nanofibers) to form a paste, which can be used in the methods described herein to form a polymer sheet having a superhydrophobic surface.

In some embodiments, the polymer used in the polymer sheet described herein does not include a hydrophilic group (e.g., OH, COOH, or NH_2). In such embodiments, the polymer used in the polymer sheet described herein is not a hydrophilic polymer or a water-soluble polymer.

In some embodiments, the polymer sheet described herein can be made from a polymer composite material. For example, the polymer sheet can further include at least one inorganic material (e.g., inorganic particles, inorganic microparticles, inorganic nanoparticles, particle agglomerates, inorganic fibers (e.g., glass fibers), or inorganic nanofibers). As used herein, the term "microparticles" generally refers to particles having an average diameter ranging from about 1 μm to about 1000 μm. As used herein, the term "nanoparticles" generally refers to particles having an average diameter ranging from about 1 nm to about 1000 nm. Examples of suitable inorganic material include SiO_2 particles (e.g., SiO_2 nanoparticles), TiO_2 particles (e.g., TiO_2 nanoparticles), Al_2O_3 particles (e.g., Al_2O_3 nanoparticles), and/or carbon particles (e.g., carbon nanoparticles) or fibers (e.g., carbon nanofibers).

In some embodiments, the polymer sheet described herein has a thickness of at least about 25 μm (e.g., at least about 50 μm, at least about 100 μm , at least about 150 μm , at least about 200 μm, at least about 250 μm, at least about 300 μm, at least about 350 μm, or at least about 400 μm) and/or at most about 1 cm (e.g., at most about 7.5 mm, at most about 5 mm, at most about 2.5 mm, at most about 1 mm, at most about 750 μm, at most about 700 μm, at most about 650 μm, or at most about 600 μm). For example, the polymer sheet can have a thickness ranging from about 200 μm to about 600 μm.

FIG. 1 is an illustration showing an exemplary method of using plate lamination for preparing a polymer sheet having a superhydrophobic surface by laminating the polymer sheet with a template. As shown in FIG. 1, a polymer sheet having a superhydrophobic surface can be prepared by first disposing a polymer sheet 10 having a surface 11 and a template 12 having a textured surface 13 between two plates 14 such that surface 11 faces textured surface 13. For example, one can first mount polymer sheet 10 on template 12 as shown in FIG. 1, and then place the article thus formed between two plates 14 so that polymer sheet 10 is in contact with one of plates 14 and template 12 is in contact with the other of plates 14.

In general, template 12 having a textured surface 13 can be a mesh, a fabric (e.g., a porous fabric), or a porous membrane, or a sandpaper. Template 12 can generally be made from any suitable material, such as a polymer (e.g., a nylon), a fabric, or a metal (e.g., stainless steel). For example, template 12 can be a metal woven mesh. In general, plates 14 can also be made from any suitable material, such as a metal (e.g., stainless steel).

In some embodiments, template 12 can be porous to allow the polymer in polymer sheet 10 to penetrate the pores to form a continuous polymer layer at the back side of template 12 and to minimize air trapped in between polymer sheet 10 and template 12. In some embodiments, template 12 (e.g., a mesh) can have an average pore size (e.g., pore diameter, pore length, or pore width) of at least about 2 µm (e.g., at least about 5 µm, at least about 10 µm, at least 25 µm, at least about 50 µm, or at least about 100 µm) to at most about 800 µm (e.g., at most about 600 µm, at most about 400 µm, at most about 200 µm, or at most about 100 µm). For example, template 12 can be a nylon mesh having a pore diameter of about 40 µm and a wire width of about 40 µm.

In some embodiments, when template 12 is a mesh, template 12 can have an average depth of pores of at least about 2 µm (e.g., at least about 5 µm, at least about 10 µm, at least 25 µm, at least about 50 µm, or at least about 100 µm) to at most about 800 µm (e.g., at most about 600 µm, at most about 400 µm, at most about 200 µm, or at most about 100 µm).

In the above embodiments, template 12 can be fully porous such that the polymer in polymer sheet 10 can infiltrate template 12 without trapping air. Without wishing to be bound by theory, it is believed that if air is trapped in template 12 (e.g., in a template made by etching holes into a silicon or metal substrate), the gas pressure would prevent the polymer from fully infiltrating into the template pattern and replicating its structure. This would create a region without the appropriate roughness and thus not fully superhydrophobic. In some embodiments, a template that has rough features but is not fully porous could be used. For example, during roll lamination, a fully porous template may not be necessary since the contact region under pressure between the polymer and template can be narrow (about 3 mm wide), which would reduce the incidence of gas being trapped. In other embodiments, the lamination process can be conducted under vacuum and there is no gas present during lamination. In such embodiments, templates with blind holes could be used without the risk of trapped gas causing surface defects.

After polymer sheet 10 and template 12 are placed between plates 14, polymer sheet 10 and template 12 can be laminated together by applying a certain pressure to plates 14 at an elevated temperature for a certain period of time.

In general, the pressure, temperature, and time required during the lamination process are sufficient to reduce the viscosity of the polymer in polymer sheet 10 such that the polymer can penetrate the pores of template 12. In some embodiments, template 12 is completely embedded in polymer sheet 10 during the lamination step such that the polymer in polymer sheet 10 forms a continuous polymer layer on the back side of template 12. In some embodiments, when the polymer in polymer sheet 10 is semicrystalline or crystalline, the lamination temperature is higher than (e.g., at least about 1°C higher than, at least about 3°C higher than, at least about 5°C higher than, at least about 10°C higher than, or at least about 50°C higher than) the melting temperature of the polymer. For example, when polymer sheet 10 is made from a LDPE having a melting point of 110°C, the lamination temperature can be about 113°C. In some embodiments, when the polymer in polymer sheet 10 is non-crystalline or amorphous, the lamination temperature is higher than (e.g., at least about 1°C higher than, at least about 3°C higher than, at least about 5°C higher than, at least about 10°C higher than, or at least about 50°C higher than) the glass transition temperature of the polymer. In some embodiments, when the polymer in polymer sheet 10 is a thermoset polymer or its precursor, the lamination temperature is higher than (e.g., at least about 1°C higher than, at least about 3°C higher than, at least about 5°C higher than, at least about 10°C higher than, or at least about 50°C higher than) softening temperature of the polymer. In some embodiments, the lamination temperature can be at least about 100°C (e.g., at least about 120°C, at least about 140°C, or at least about 160°C) and/or at most about 250°C (e.g., at most about 220°C, at most about 200°C, or at most about 180°C). Without wishing to be bound by theory, it is believed that, if the lamination temperature is too low (e.g., lower than the melting temperature of the polymer), the polymer in polymer sheet 10 may not flow through the pores of template 12 to form a continuous layer on the back side of template and therefore the polymer may not be stretched and torn when template 12 is peeled off polymer sheet 10. As a result, the aspect ratio of the embossed features may not be sufficient to create roughness adequate to allow surface 11 to exhibit superhydrophobicity.

In some embodiments, the lamination pressure can be at least about 0.5 psi (e.g., at least about 1 psi, at least about 5 psi, at least about 10 psi, at least about 20 psi, at least about 30 psi, at least about 50 psi, at least about 100 psi, or at least about 200 psi) and/or at most about 10000 psi (e.g., at most about 8000 psi, at most about 7000 psi, at most about 6000 psi, at most about 5000 psi, at most about 2500 psi, or at most about 1000 psi).

In some embodiments, the lamination time is at least about 0.1 second (e.g., at least about 0.5 second, at least about 1 second, at least about 30 seconds, or at least about 1 minute) and/or at most about 2 hours (e.g., at most about 1.5 hours, at most about 1 hour, at most about 45 minutes, at most about 30 minutes, at most about 15 minutes, at most about 10 minutes, or at most about 5 minutes).

After the lamination process, the laminated material (i.e., polymer sheet 10 laminated with template 12) can generally be cooled down to a suitable temperature (e.g., room temperature such as 25°C) in air. In some embodiments, when the polymer in polymer sheet 10 is semicrystalline or crystalline, the laminated material can be cooled below the melting temperature of the polymer before separating polymer sheet 10 and template 12. In some embodiments, polymer sheet 10 and template 12 can be separated at a temperature above the glass transition temperature or softening temperature of the polymer in polymer sheet 10 as it can be difficult to separate them below its glass transition or softening temperature when polymer sheet 10 hardens. Without wishing to be bound by theory, it is believed that plates 14 can be easily removed as no chemical bonds are formed between polymer sheet 10 and plate 14 or between template 12 and plate 14.

In general, after template 12 is separated from polymer sheet 10 (e.g., by peeling template 12 from polymer sheet 10), surface 11 on polymer sheet 10 is converted into a superhydrophobic surface 19 (e.g., having a water contact angle of at least about 150°). Without wishing to be bound by theory, it is believed that, because the polymer in polymer sheet 10 penetrates the pores in template 12 during the lamination process, template 12 is at least partially embedded by the polymer at surface 11 of polymer sheet 10. As a result, peeling off template 12 from polymer sheet 10 gives surface 11 a sufficient roughness, thereby converting surface 11 into a superhydrophobic surface 19. Further, without wishing to be bound by theory, it is believed that the roughness on surface 19 can be caused by the pores in template 12 (i.e., as the polymer in polymer sheet 10 penetrates the pores during lamination) and/or the roughness of the material (e.g., the wires, filaments, or fabrics) that forms template 12.

In some embodiments, template 12 can be coated with a layer of inorganic nanoparticles before template 12 is laminated with polymer sheet 10. Template 12 thus formed can then be used to form a superhydrophobic surface on polymer sheet 10 by using the same method shown in FIG. 1.

Examples of suitable inorganic nanoparticles that can be coated onto template 12 include SiO_2 nanoparticles, TiO_2 nanoparticles, Al_2O_3 nanoparticles, and carbon nanoparticles. In some embodiments, the inorganic nanoparticles can have an average diameter of at least about 3 nm (e.g., at least about 5 nm, at least about 10 nm, at least about 30 nm, at least about 50 nm, at least about 100 nm, or at least about 150 nm) and/or at most about 1000 nm (e.g., at most about 800 nm, at most about 600 nm, at most about 400 nm, or at most about 300 nm).

In some embodiments, the inorganic nanoparticles can be surface treated (e.g., by reacting the nanoparticles with a suitable agent such as silane) to reduce their hydrophilicity. An example of such inorganic nanoparticles is silane-treated SiO_2 nanoparticles.

In some embodiments, the inorganic nanoparticles can be coated onto template 12 by a method known in the art. For example, the coating can be carried out by dispersing the inorganic nanoparticles in an aqueous solvent (e.g., water or a mixture of water and an alcohol such as methanol) to form a dispersion, applying the dispersion onto template 12, and drying the dispersion. As another example, the inorganic nanoparticles can be disposed directly on template 12 in a solid form (e.g., as a powder).

Without wishing to be bound by theory, it is believed that the inorganic nanoparticles on template 12 can generate nanostructures on surface 11 of polymer sheet 10, thereby adding additional roughness on surface 11 and facilitating formation of a superhydrophobic surface. In addition, without wishing to be bound by theory, it is believed that surface 11 treated with template 12 coated with a layer of inorganic nanoparticles can have improved superhydrophobic properties (e.g., an increased water contact angle or an decreased water slip-off angle), improved abrasion resistance, and improved water pressure resistance.

In some embodiments, the lamination pressure described above depends on whether template 12 or polymer sheet 10 is coated with a layer of nanoparticles. When template 12 or polymer sheet 10 is coated with a layer of nanoparticles, without wishing to be bound by theory, it is believed that, if the lamination pressure is too high (e.g., more than 10,000 psi), the extent of polymer infiltration into the porous nanoparticle layer could be significantly increased and can force the nanoparticles to be fully embedded into the polymer sheet, thereby reducing the roughness (e.g., the micro-texture at a scale of about 100 microns) generated by the nanoparticles on the surface of the polymer sheet, which reduces the hydrophobicity of the surface. Further, in such embodiments, without wishing to be bound by theory, it is believed that, if the lamination pressure is too low (e.g., lower than 0.5 psi), the nanoparticles are not embedded into the polymer sheet, thereby reducing the roughness generated by the nanoparticles on the surface of the polymer sheet.

In general, a polymer sheet having a superhydrophobic surface (e.g., having a water contact angle of at least about 150°) can also be prepared by laminating the polymer sheet with a layer of a nanomaterial (e.g., nanoparticles or nanofibers). In such embodiments, the lamination process can be performed by plate lamination, autoclave lamination, or roll lamination.

FIG. 2 is an illustration showing an exemplary method of using plate lamination for preparing a polymer sheet having a superhydrophobic surface by laminating the polymer sheet with a layer of a nanomaterial. As shown in FIG. 2, a polymer sheet having a superhydrophobic surface can be prepared by first disposing a polymer sheet 20 having a surface 21 and a layer 22 containing a nanomaterial (e.g., nanoparticles or nanofibers) between two plates 24. For example, one can apply layer 22 onto one of plates 24, and then sequentially place polymer sheet 20 and the other of plates 24 on top of layer 22 so that polymer sheet 20 is in contact with layer 22 and one of plates 24.

In some embodiments, polymer sheet 20 and plates 24 can be the same as those described above in FIG. 1. In some embodiments, when layer 20 includes inorganic nanoparticles (e.g., SiO_2 nanoparticles or TiO_2 nanoparticles), the inorganic nanoparticles can be the same as those described in connection with the methods shown in FIG. 1 above.

Layer 22 can generally be disposed on one of plates 24 by a known method. For example, layer 22 can be disposed on one of plates 24 by dispersing a nanomaterial (e.g., nanoparticles or nanofibers) in an aqueous solvent (e.g., water or a mixture of water and an alcohol such as methanol) to form a dispersion, disposing the dispersion onto one of plates 24, and then drying the dispersion. As another example, layer 22 can be disposed on one of plates 24 by directly applying a nanomaterial in a solid form (e.g., as a powder) onto plate 24. In such embodiments, plate 24 can be covered by a substrate having a textured surface (e.g., a piece of paper or a rigid substrate having a textured surface) onto which the solid nanomaterial can be applied. In general, layer 22 thus formed is porous such that the polymer in polymer sheet 20 can penetrate the pores in layer 22 during the lamination process. Without wishing to be bound by theory, it is believed that using a substrate having a textured surface to cover plate 24 can facilitate retaining the nanomaterial on plate 24 and/or can impart a large scale of surface roughness to surface 21 on polymer sheet 20, which can improve the superhydrophobic properties after a superhydrophobic surface is formed. In some embodiments, layer 22 can be disposed (e.g., by a solution coating or coating in a solid form) on polymer sheet 20. The coated polymer sheet can then be disposed between two plates 24 before lamination.

In general, layer 22 can have any suitable thickness. In some embodiments, layer 22 can have a thickness of at least about 1 μm (e.g., at least about 5 μm, at least about 10 μm, at least about 20 μm, or at least about 40 μm) and/or at most about 5 nm (e.g., at most about 3 mm, at most about 1 mm, at most about 500 μm, at most about 100 μm, at most about 70 μm, at most about 60 μm, or at most about 50 μm).

After polymer sheet 20 and layer 22 are placed between plates 24, polymer sheet 20 and layer 22 can be laminated together by applying a certain pressure to plates 24 at an elevated temperature for a certain period of time. In general, the pressure, temperature, and time required during the lamination process are sufficient to allow the polymer in polymer sheet 20 to penetrate into the pores of the nanomaterial (e.g., nanoparticles) such that at least some of the nanomaterial is partially embedded in polymer sheet 20 and partially exposed to air on surface 21. In some embodiments, the lamination temperature is higher than (e.g., at least about 1°C higher than, at least about 3°C higher than, at least about 5°C higher than, at least about 10°C higher than) the melting temperature (or the glass transition or softening temperature) of the polymer in polymer sheet 20. For example, when polymer sheet 20 is made from a LDPE having a melting point of 119°C, the lamination temperature can be from about 120°C to about 130°C. In some embodiments, the lamination temperature can be at least about 100°C (e.g., at least about 120°C, at least about 140°C, or at least about 160°C) and/or at most about 250°C (e.g., at most about 220°C, at most about 200°C, or at most about 180°C). In some embodiments, the lamination time and pressure can be the same as those described in connection with the methods shown in FIG. 1 above.

After the lamination process, the laminated material (i.e., polymer sheet 20 laminated with layer 22) can generally be cooled down to a suitable temperature in air. For example, the laminated material can be cooled down to a temperature below the melting temperature but above the glass transition temperature of the polymer in polymer sheet 20. Plates 24 can subsequently be removed to form polymer sheet having a superhydrophobic surface 29. Without wishing to be bound by theory, it is believed that plates 24 can be easily removed as no chemical bonds are formed between polymer sheet 20 and plate 24 or between layer 22 and plate 24. In addition, without wishing to be bound by theory, it is believed that, as layer 22 does not include a template and the nanomaterial in layer 22 is embedded in (i.e., partially or fully) polymer sheet 20, no addition step (e.g., peeling off a template as shown in FIG. 1) is needed to form a superhydrophobic surface on polymer sheet 20.

In some embodiments, a polymer sheet having a superhydrophobic surface can be prepared by using roll lamination to laminate the polymer sheet together with a layer of a nanomaterial. FIG. 3(a) is an illustration showing an exemplary method of such an embodiment. As shown in FIG. 3(a), while polymer sheet 30 having surface 31 is being fed between upper and lower rollers 34, a nanomaterial 32 (e.g., nanoparticles or nanofibers) in a container (e.g., a box) can be absorbed onto the surface of a lower roller 34 and then laminated onto polymer sheet 30 at the nip section of rollers 34. After the roll lamination is completed, surface 31 is generally converted into superhydrophobic surface 39. In some embodiments, polymer sheet 30 and nanomaterial 32 can be the same as those described with respect to FIG. 2 above.

In some embodiments, roll lamination can be carried out by feeding a carrier film (e.g., kraft paper) coated with a nanomaterial (e.g., nanoparticles or nanofibers) into two rollers at the same time as a polymer sheet such that the nanomaterial on the carrier film faces the polymer sheet. As a result, the carrier film and polymer sheet are laminated together in the nip section. After exiting the nip, the carrier film and the polymer sheet can be separated to form a polymer sheet having a superhydrophobic surface, which can be then be rolled onto a roller separately from the carrier film and stored for future use. In some embodiments, the roll lamination described above can be carried out in a roll-to-roll method.

FIG. 3(b) is an illustration showing another exemplary roll lamination process. As shown in FIG. 3(b), roll lamination can be carried out by coating a solution (e.g. with a solvent containing water or a mixture of water and an alcohol, or other suitable solvents) of nanoparticles 33 stored in coater 32 onto polymer sheet 30 to form a nanoparticle layer 35 on polymer surface 31. The solution is then passed through a drying stage 36 to remove the solvent, thereby forming layer 37 containing dried and porous nanoparticles. The coated polymer sheet 30 is then brought into a laminator having upper and lower rollers 34. Upon applying heat and pressure, the polymer in polymer sheet 30 flows into the pores between nanoparticles in layer 37 to create a superhydrophobic surface 9. In some embodiments, a release layer 38 can be placed between layer 37 and upper roller 34 to prevent the nanoparticles in layer 37 from adhering onto upper roller 34. Similarly, a second release layer 38 can be placed between polymer sheet 30 and lower roller 34 to prevent polymer 30 from adhering onto lower roller 34.

In some embodiments, the nanomaterial used in the methods shown in FIG. 2 can be coated onto a template (e.g., a mesh or a fabric) before being laminated with a polymer sheet. FIG. 4 is an illustration showing an exemplary method of using plate lamination for preparing a polymer sheet having a superhydrophobic surface by laminating the polymer sheet with a template coated a layer of a nanomaterial. As shown in FIG. 4, a polymer sheet having a superhydrophobic surface can be prepared by first disposing a polymer sheet 40 having a surface 41 and a template 42 coated with a layer 46 containing a nanomaterial (e.g., nanoparticles or nanofibers) between two plates 44 such that surface 41 faces layer 46. Optionally, polymer sheet 40 can also be coated with a layer 45 containing a nanomaterial (e.g., nanoparticles or nanofibers). Polymer sheet 40 can then be laminated with layer 46 on template 42 to form a superhydrophobic surface 49 using the same approach as the methods described in connection with FIG. 1 (e.g., laminating the polymer sheet with the template, cooling the laminated material, and separating the template from the polymer sheet). In some embodiments, polymer sheet 40, template 42, and nanomaterials in layers 45 and 46 can the same as those described in connection with FIG. 1 above. In addition, in some embodiments, the lamination process (including lamination pressure, temperature, and time) can also be the same as those described in connection with FIG. 1 above.

In some embodiments, layer 45 can have a thickness of at least about 1 µm (e.g., at least about 5 µm, at least about 10 µm, at least about 20 µm, or at least about 40 µm) and/or at most about 800 µm (e.g., at most about 700 µm, at most about 600 µm, at most about 500 µm, at most about 300 µm, at most about 100 µm, or at most about 50 µm).

In some embodiments, during the lamination process, template 42 is embossed into surface 41 on polymer sheet 40 without allowing the polymer in polymer sheet 40 to penetrate the pores in template 42 and form a continuous polymer film on the back side of the template. Such an embossing process can be achieved by adjusting the lamination pressure and temperature, and can form a negative image of template 42 on surface 41, which can provide micro-sized patterns. Without wishing to be bound by theory, it is believed that such a process can create both large scale roughness (i.e., by embossing polymer sheeting 40 with template 42) and small scale roughness (i.e., by allowing the polymer in polymer sheet 40 to infiltrate into the pores in the nanoparticles on template 42 or on polymer sheet 40) on surface 41, which can improve abrasion resistance of the resulting superhydrophobic surface 49.

Without wishing to be bound by theory, it is believed that the polymer in polymer sheet 40 can flow into the pores between nanomaterials in layers 45 and 46 during the lamination process so that at least some of the nanomaterials are partially embedded and partially exposed in polymer sheet 40, thereby forming micro-sized roughness that facilitates formation of a superhydrophobic surface. In addition, micro-sized patterns on surface 41 formed by template 42 can also facilitate formation of a superhydrophobic surface. Without wishing to be bound by theory, it is believed that using a template coated with a layer of a nanomaterial can significantly improve the mechanical properties, abrasion resistance, and water pressure resistance of a superhydrophobic surface.

Without wishing to be bound by theory, it is believed that one advantage of the methods described herein is that these methods are completely free of organic solvents or toxic chemicals and therefore are environmentally friendly. Further, without wishing to be bound by theory, it is believed that another advantage of the methods described herein is that, since the template (e.g., a mesh) used in these methods is commercially available in a large format (e.g., more than 1 meter wide and/or more than hundreds of meters long), these methods can be used to manufacture superhydrophobic surfaces on a large scale. In addition, without wishing to be bound by theory, it is believed that another advantage of the methods described herein is that the template (e.g., a mesh) used in these methods can be reused and therefore can reduce production costs.

In some embodiments, the polymer sheet prepared by the methods described herein can have a hydrophobic surface that has a plurality of protrusions. In some embodiments, the protrusions can have an average length or width of at least about 2 μm (e.g., at least about 5 μm, at least about 10 μm, at least about 20 μm, or at least about 50 μm) and/or at most about 500 μm (e.g., at most about 400 μm, at most about 300 μm, at most about 200 μm, or at most about 100 μm). As used herein, the length or width of a protrusion refers to that measured substantially parallel to the surface of the polymer sheet. In some embodiments, the protrusions can have an average height of at least about 25 μm (e.g., at least about 50 μm, at least about 100 μm, at least about 200 μm, or at least about 500 μm) and/or at most about 1000 μm (e.g., at most about 900 μm, at most about 800 μm, at most about 700 μm, or at most about 600 μm). As used herein, the height of a protrusion refers to that measured substantially perpendicular to the surface of the polymer sheet. In some embodiments, the protrusions can have an average distance of at least about 5 μm (e.g., at least about 10 μm, at least about 20 μm, or at least about 50 μm) and/or at most about 500 μm (e.g., at most about 400 μm, at most about 300 μm, at most about 200 μm, or at most about 100 μm) between two neighboring protrusions. In some embodiments, the distance between protrusions is substantially the same across the surface. In some embodiments, the pattern of a template is replicated substantially uniformly across the surface.

In some embodiments, when a polymer sheet having a superhydrophobic surface is prepared by the methods shown in FIG. 1, the protrusions can be generated by penetration of the polymer in the polymer sheet into the pores of the template during the hot lamination process and then removal of the template. In some embodiments, when nanoparticles are used to prepare a superhydrophobic surface on a polymer sheet (e.g., as shown in FIG. 2), the protrusions can be formed from the nanoparticles partially embedded in the polymer sheet.

In some embodiments, when both a template and nanoparticles are used to prepare a superhydrophobic surface on a polymer sheet (e.g., as shown in FIG. 4), the protrusions can be formed from both the polymer in the polymer sheet and the nanoparticles partially embedded in the polymer sheet. FIG. 5 illustrates an exemplary polymer sheet prepared by the methods shown in FIG. 4 when template 42 is coated with a layer of nanoparticles. As shown in FIG. 5, polymer sheet 50 has a superhydrophobic surface 51 and includes a layer of nanoparticles 52. At least some of the nanoparticles 52 are partially embedded in polymer sheet 50 and are partially exposed to air on surface 51. Surface 51 has a plurality of protrusions, each of which has a top surface 53 and a side wall 55. In addition, polymer sheet has a surface 57 between two neighboring protrusions. Nanoparticles 52 are disposed on top surface 53, side wall 55, and surface 57 between two neighboring protrusions. In some embodiments, surface 57 between two neighboring protrusions and top surface 53 of each protrusion have an average distance of at least about 2 μm (e.g., at least about 5 μm, at least about 10 μm, at least about 20 μm, at least about 30 μm, at least about 50 μm, at least about 75 μm, or at least about 100 μm) and/or at most about 800 μm (e.g., at most about 700 μm, at most about 600 μm, at most about 500 μm, at most about 450 μm, at most about 400 μm, at most about 350 μm, or at most about 300 μm). Without wishing to be bound by theory, it is believed that, if surface 51 is scratched, although nanoparticles 52 on top surface 53 may be removed by scratching, nanoparticles 52 on side wall 55 and surface 57 can remain on surface 51. Thus, nanoparticles 52 partially embedded on surfaces 55 and 57 can significantly improve the abrasion resistance and water pressure resistance of surface 51.

FIG. 6 illustrates another exemplary polymer sheet prepared by the methods shown in FIG. 4 when template 42 is coated with a layer of nanoparticles. As shown in FIG. 6, polymer sheet 60 has a superhydrophobic surface 61 and includes a layer of nanoparticles 62. At least some of the nanoparticles 62 are partially embedded in polymer sheet 60 and are partially exposed to air on surface 61. Surface 61 has a plurality of protrusions, each of which has a top surface 63 and a side wall 65. In addition, polymer sheet has a surface 67 between two neighboring protrusions. Nanoparticles 62 are disposed on top surface 63, side wall 65, and surface 67 between two neighboring protrusions.

In some embodiments, the polymer sheet prepared by the methods described herein can have superhydrophobicity. For example, the polymer sheet prepared by the methods disclosed herein can have a hydrophobic surface that has a water contact angle of at least about 150° (e.g., at least about 155°, at least about 160°, at least about 165°, at least about 170°, or at least about 175°) and/or at most about 179° (e.g., at most about 175°, at most about 170°, at most about 165°, or at most about 160°).

In some embodiments, the polymer sheet prepared by the methods described herein can have a hydrophobic surface that has a water slip-off angle of at most about 10° (e.g., at most about 5°, at most about 4°, at most about 3°, at most about 2°, or at most about 1°) and/or at least about 0.1° (e.g., at least about 0.5°, at least about 1°, at least about 1.5°, at least about 2°, or at least about 2.5°).

In some embodiments, the polymer sheet prepared by the methods disclosed herein can have superior abrasion resistance. For example, the polymer sheet prepared by the methods disclosed herein can have a hydrophobic surface that has a water contact angle of at least about 150° (e.g., at least about 155°, at least about 160°, at least about 165°, at least about 170°, or at least about 175°) after 1,000 abrasion cycles (e.g., after 5,000 abrasion cycles, after 10,000 abrasion cycles, after 50,000 abrasion cycles, or after 100,000 abrasion cycles) under a pressure of 32 KPa. As another example, the polymer sheet prepared by the methods disclosed herein can have a hydrophobic surface that has a water contact angle of at least about 150° (e.g., at least about 155°, at least about 160°, at least about 165°, at least about 170°, or at least about 175°) after the hydrophobic surface is scratched by a steel nail at least 10 times (e.g., after 20 times, after 30 times, after 40 times, or after 50 times). In some embodiments, the polymer sheet prepared by the methods disclosed herein can be touched or handled by hand without damaging its superhydrophobic surface.

In some embodiments, the polymer sheet prepared by the methods described herein can have superior static water pressure resistance. For example, the polymer sheet prepared by the methods disclosed herein can have a hydrophobic surface that remains dry (e.g., having a layer of air between the superhydrophobic surface and water) under a water pressure of at least about 8 psi (e.g., at least about 10 psi, at least about 20 psi, at least about 40 psi, at least about 60 psi, or at least about 85 psi) for at least about 5 hours (e.g., at least about 10 hours, at least about 20 hours, at least about 30 hours, at least about 40 hours, or at least about 50 hours).

In some embodiments, the polymer sheet prepared by the methods described herein can have superior dynamic water pressure resistance. For example, the polymer sheet prepared by the methods disclosed herein can have a hydrophobic surface that remains dry upon impact of a water droplet at a speed of at least about 5 m/s (e.g., at least about 6 m/s, at least about 7 m/s, at least about 8 m/s, at least about 9 m/s, or at least about 10 m/s).

While a free-standing polymer sheet has been described as an example on which a superhydrophobic surface can be formed, the methods described herein can also be used to form a superhydrophobic surface on other substrates. For example, the methods described herein can be used to form a superhydrophobic surface on a free-standing polymer sheet or film first. The free-standing polymer film or sheet thus formed can then be adhered to the surface of another substrate (e.g., a metal, glass, polymer or ceramic substrate) by using an adhesive to form a composite material having a superhydrophobic surface. In some embodiments, the methods described above can be used to directly form a superhydrophobic surface on a polymer layer coated or adhered on a substrate (e.g., a metal, glass, polymer or ceramic substrate) to form a composite material having a superhydrophobic surface.

The superhydrophobic surface prepared by the methods described herein can be used in food-processing equipment due to its excellent non-wetting, self-cleaning properties. In addition, the superhydrophobic surface prepared by the methods described herein can be used in roofing, wind turbines, aircraft, and naval structures due to its excellent ice-repellent properties.

The contents of all publications cited herein (e.g., patents, patent application publications, and articles) are hereby incorporated by reference in their entirety.

The following examples are illustrative and not intended to be limiting.

Example 1: Fabricating polymer sheets having a superhydrophobic surface by using a template

Materials, methods and surface fabrication: A commercially available thermoplastic sheet of low density polyethylene (LDPE) manufactured by Berry Plastics (Evansville, IN) from 97% recycled polyethylene, 2% calcium carbonate and 1% slip oleamide and sold through McMaster-Carr was used as the polymer substrate. The thickness of the LDPE film was 100 μm and 10 layers of the LDPE film were used at each time to make free-standing superhydrophobic sheets that were approximately 1 mm thick. The polymer film softens at 106 °C and melts over the range from 113-120 °C Three types of stainless steel mesh (i.e., M1, M2, and M3) and one type of nylon mesh (i.e., M4) (all from McMaster-Carr) with different wire diameters and pore sizes were used as templates. The structures and details of the mesh are shown in Table 1 below.

Table 1. Parameters of mesh templates for fabricating superhydrophobic surfaces.

Mesh NO.	Wire Diameter 1 (μm)	Wire Diameter 2 (μm)	Square pore side length (μm)	Open Area (%)
M1, 325 mesh	28	28	50	41
M2, 400 mesh	25	25	38	36
M3, 200 ×1400 mesh	71	41	10	2
M4, 371 mesh	33	33	36	28

The procedure for fabricating superhydrophobic surfaces involved two processing steps. In the first step, a stack of LDPE sheets and a mesh template are laminated together under heat and pressure with the targeted polymer surface facing the mesh template. The stack-up was heated above its softening temperature under pressure for 3-30 minutes. The laminated stack was then cooled to 25°C. In the second step, the mesh template was separated from the polymer film by peeling. The superhydrophobic surface was formed and exposed during the peeling process. As the LDPE did not adhere to the stainless steel or Nylon mesh, the template could be reused. The fabrication conditions of the above process are summarized in Table 2.

Table 2. Fabrication conditions for surface 1-4 and their superhydrophobic properties.

Surface	**Mesh**	**Lamination Conditions**			**Peel Temp**	**Superhydrophobicity**			
#	#	Temp °C	Pressure kPa	Time Min	°C	θ_{Static}	θ_{Adv}	θ_{Rec}	θ_{Slip}
S1	M1	115	1400	30	25	125°	-	-	-
S2	M1	120	1400	30	25	160°	-	-	3°
S3	M1	125	1400	3	25	160°	-	-	5°
S4	M2	125	69	15	25	160°	163°	155°	5°
S5	M3	125	69	15	25	158°	-	-	3°
S6	M4	125	69	15	25	160°	162°	157°	5°

Characterization: The surface structures were studied by field emission scanning electron microscopy (FESEM, Amary) and optical microscopy (Nikon-SMZ 1500 and Laborlux-12ME). The SEM images are shown in FIGs. 7 and 8.

The static contact angles (CAs) and roll-off angle were measured with a goniometer (250-F1, Rame-Hart Instruments Co). Droplets of distilled water, with a volume of 2-5 μL, were placed gently onto the surface at room temperature and pressure. The static CA and advancing and receding CAs were measured five times at different locations such that the measurement variance was ± 2°. The slip-off angle was determined by measuring the substrate angle at which water droplets (~10 μL) placed on the surface with a micro syringe needle would roll-off the surface. The results are summarized in Table 2. As shown in Table 2, surfaces S2-S6 were superhydrophobic surfaces having a water contact angle ranging from 158-160° and a water slip-off angle less than 5°. Without wishing to be bound by theory, it is believed that S1 did not form a superhydrophobic surface because the lamination temperature was not sufficiently high to allow the mesh template to be fully embedded into the LDPE. Since the polymer did not flow through the pores of the mesh, the polymer was not stretched and torn when the mesh was peeled off the polymer. As a result, the aspect ratio of the embossed features is not sufficient to create roughness adequate to exhibit superhydrophobicity.

Abrasion tests: First, the surfaces S2-S6 were assessed qualitatively by simply pressing with a bare hand. It was found that the superhydrophobicity of surfaces S2 and S5 decreased dramatically as water droplets were pinned in the touched area, while the superhydrophobicity of surfaces S3, S4 and S6 remained unchanged after pressing with a bare hand as shown in FIG. 9a (surface S6). Without wishing to be bound by theory, it is believed that the relative lack of stability of surfaces S2 and S5 may be due to the fact that S2 had relatively thin petal-like features, whereas S5 had a very low concentration of small features. By contrast, without wishing to be bound by theory, it is believed that surfaces S3, S4 and S6 had a superior stability as they had a higher surface density of larger, higher aspect ratio features.

The chemical and abrasion resistance of surfaces S4 and S6 was then studied further using a manual, multi-step test that includes a sequence of four steps: (1) dry abrading firmly with a gloved hand (Showa Best Glove part# 6005PF) using a back and forth movement for 50 times, (2) dry abrading firmly with a hand wearing an industrial cotton glove back and forth for 50 times, (3) wet scrubbing manually with a gloved finger for 1 hour (20 cycles @ 2-4 minutes/cycle) with a saturated industrial cleaner solution (ALCONOX - Powdered Precision Cleaner, containing 7-13% sodium carbonate, 10-30% sodium dodecylbenzenesulfonate, 10-30% tetrasodium pyrophosphate, and 10-30% sodium phosphate), and (4) ultrasonicating in the same saturated industrial cleaner solution for 5 hours (Branson 1200 ultrasonic cleaner, ~150 watts). After this sequence of tests, the surfaces were rinsed with tap water and dried with filtered dry compressed air. Unexpectedly, the superhydrophobicity of surfaces S4 and S6 remained unchanged. As shown in FIG. 9(b), two water droplets maintained a spherical shape on surface S6, which had been only partially dried with compressed air after testing. The static water contact angles of surfaces S4 and S6 remained essentially unchanged as shown in FIG. 9(c). The slip-off angles of 10 μL water droplets on surfaces S4 and S6 increased slightly from 5° to 10°. Without wishing to be bound by theory, it is believed that the increased slip-off angle may result from a partial disordering of the polymer protrusions after these abrading and scrubbing tests as shown in FIG. 9(d). The disorder would result in protrusions of varying heights and therefore at least some protrusions may be partially wetted by water droplets.

A mechanized abrasion test was conducted with a Taber model 5900 reciprocating abraser using a CS-8 WEARASER abradant to measure the abrasion resistance of surface S4. The following conditions were used for the abrasion test: the stroke length was 4 cm, the abrasion linear speed was 8 $cm \cdot s^{-1}$, and the applied pressure was 32.0 kPa (4.64 psi). The change in static contact angle on surface S4 with increasing abrasion cycles is shown in FIG. 10(a). As seen in this figure, the static contact angle remained essentially unchanged at 160° over the first 2520 abrasion cycles and then decreased slowly to 155° with increasing cycles. The slip-off angle remained unchanged after 2520 cycles and increased slowly with increasing abrasion cycles. After 5520 cycles, water droplets on the surface still appear as transparent balls (as shown in FIG. 10(b)). When the total number of abrasion cycles was increased to 6520, the contact angle decreased to 140° and then maintained this level with further abrasion cycles. Both the manual multi-step test and the mechanized reciprocating test demonstrate that the superhydrophobic surfaces possess good mechanical and chemical stability as well as excellent abrasion resistance.

Water pressure stability test: The water pressure stability of surface S2 was tested as follows: A piece of the fabricated superhydrophobic polymer sheet with a size of 25 mm × 38 mm was placed inside a Nordson-EFD polypropylene syringe barrel, immersed in water, and capped with a piston. The syringe was then pressurized, using a Nordson-EFD regulated dispenser. The reflectivity at the interface between water and the superhydrophobic surface was monitored visually and recorded using a digital camera. After the pressure was relieved, the sample was removed from the water filled syringe and the wetting properties of the surface were measured using optical microscopy (Nikon-SMZ 1500 and Laborlux-12ME).

The results showed that, the reflectivity remained relatively stable to 140 kPa of applied pressure, but the reflected intensity gradually became weaker with increasing pressure. The reflective interface significantly faded when the applied pressure was increased to 550 kPa over a period of 90 seconds. In addition, the results show that, at a lower pressure of 55 kPa (i.e., 8 psi or the pressure at a depth of 5.6 m of water), surface S2 remained completely dry when it was removed after 5 hours of under-water immersion. In sum, the water pressure stability of the superhydrophobic surfaces described herein is significantly better than that of lotus leaves, as well as other reported polymeric superhydrophobic surfaces.

Example 2: Fabricating polymer sheets having a superhydrophobic surface by using a porous nanoparticle layer

Ultra-high-molecular-weight polyethylene (UHMWPE, McMaster Carr, Elmhurst, IL), was used as the polymer substrate as it is a well-known tough material with high abrasion resistance, a high level of crystallinity (up to 85%), and the highest impact strength of any thermoplastic polymer. In addition, the high melt viscosity limits the infiltration of the UHMWPE into the porous nanoparticle layer, thereby minimizing the number of particles engulfed (i.e., fully embedded) into the polymer during the lamination process. Experiments were conducted to characterize the effect of the lamination pressure on the morphology and wetting properties of UHMWPE nanocomposite surfaces prepared by the percolative infiltration of the polymer into the porous nanoparticle layer

A total of nine samples were prepared under different conditions. Sample 1 was an original, untreated UHMEPE sheet. Sample 2 was made by heating a UHMWPE sheet to 154.4°C for 30 minutes to melt the crystalline polymer without applying any pressure, and then cooling it to room temperature in air. Sample 3 was made by heating a UHMWPE sheet covered by a layer of nanoparticles (3 mm thick) to 154.4°C for 30 minutes without applying any pressure, and then cooling to room temperature in air. Samples 4-9 were made by heating a UHMWPE sheet covered by a layer of nanoparticles (3 mm thick) to 154.4°C for 30 minutes while being laminated under a pressure of 83 psi, 830 psi, 3,000 psi, 5,000 psi, 8,000 psi and 13,000psi, respectively, and then cooling it to room temperature in air.

The lamination conditions and hydrophobic properties of these samples are shown in Table 3. The SEM images of the polymer sheet formed in Samples 1-4 and 8 are shown in FIGs. 11-13.

Table 3. Water contact angles and slip-off angles on different samples

Samples# and Conditions	Water contact angle	Slip-off angle of droplets of 8μL
1. Original UHMW PE	105±2°	Not slip,
2. Heating and Cooling	123±2°	Not slip,
3. Heating and Cooling under the covering of Nanoparticles	153±2°	30°±2°
4. Laminating at 83 psi	170±2°	~0
5. Laminating at 830 psi	170±2°	~0
6. Laminating at 3000 psi	170±2°	~0
7. Laminating at 5000 psi	170±2°	~0
8. Laminating at 8,000 psi	149±2°	25°±2°
9. Laminating at 13,000 psi	135±2°	Not slip

As shown in FIGs 11(a) and (b), the original untreated UHMWPE substrate in Sample 1 was relatively flat with striations from the extrusion process remaining on the surface. The surface became more highly structured after heating in Sample 2 as shown in FIGs 11(c) and (d). The recrystallization of UHMWPE occurred under these conditions, forming micro bumps on the order of 100 microns as shown in these figures. Static water contact angles on Samples 1 and 2 were 105±2° and 123±2°, respectively. The higher static water contact angle for the heat treated surface was consistent with increased roughness based on the Wenzel equation known in the art. As shown in Table 3, small water droplets could not slip off the surface of either Sample 1 or 2. Thus, no superhydrophobicity was observed for these two samples and their surfaces could be fully wetted.

In Sample 3, a layer of hydrophobic silica nanoparticles (TS 530, Cabot Corporation) was used to cover the polymer substrate and the assembly was heated using the same conditions as those used in treating the neat UHMWPE substrate in

Sample 2. As shown in FIGs 11(e) and (f), the nanoparticles decorated the polymer substrate after heating. A surface structure similar to the uncoated polymer was observed, however nanoparticles created an additional fine-scale roughness. Indeed, the underlying polymer micro-texture was revealed by removing the nanoparticles by etching in a 49% HF for 8 hours. As shown in FIGs 11(g) and (h), UHMWPE not coated with nanoparticles showed a similar micro-texture to that observed in the UHMWPE not coated with nanoparticles (comparing FIG. 11(c) with 11(g)), while the presence of nanoparticles created a layer of fine-scale roughness (comparing FIG. 11(d) and (h)). Thus, even without applied pressure, percolative infiltration of UHMW PE into nanoparticles could be observed. As a result, Sample 3 exhibited superhydrophobicity as evidenced by a water contact angle of 153±2°, but some wetting could occur in Sample 3 as small water droplets could not slip off the surface.

To further investigate the effect of process conditions of the percolative infiltration of UHMWPE into nanoparticles for the control of hierarchical surface structures, pressure was applied during heating. SEM images of samples made under different pressures are shown in FIGs 12 and 13. The same method of wet etching was applied to remove the nanoparticles after lamination so as to more clearly observe the underlying polymer structures. At a relatively low pressure of 83 psi, micro bumps (on the order of 100 microns) that formed during the recrystallization of UHMWPE could still be detected on the surface in Sample 4 (FIG. 12(a)). However, any micro-cracks were effectively eliminated. After etching away the embedded nanoparticles, micro bumps on the order of 10 microns with fine nanostructures were revealed (as shown in FIGs 12(b)-(d)). This nanostructure was far more extensive than that observed when no pressure is applied (as shown in FIGs. 11(g) and (h)), indicating the enhanced percolation length of UHMWPE under pressure. The surface in Sample 4 prepared at 83 psi exhibited excellent superhydrophobic properties with a contact angle of about 170° and a slip-off angle of about 0°. Water droplets less than 5 μL could not be placed onto the surface from a steel micro syringe tip, and larger water droplets could easily slip off the surface. Similar properties were observed for Sample 5 prepared at 830 psi.

As shown in Table 3, polymer sheets prepared by lamination at 83 psi, 830 psi, 3000 psi, and 5000 psi (i.e., in Samples 4-7) exhibited the best superhydrophobic properties among the nine samples. Without wishing to be bound by theory, it is believed that further increasing the lamination pressure could increase the extent of polymer percolation into the porous nanoparticle layer and could force the nanoparticles to be fully embedded into the polymer sheet, thereby reducing the roughness (e.g., the micro-texture at a scale of about 100 microns) generated by the nanoparticles on the surface of the polymer sheet. As a result, at higher lamination pressures, the superhydrophobic properties of the polymer sheets began to become adversely affected with a decrease in the contact angle and an increase in the slip-off angle as shown in Table 3. Specifically, when the lamination pressure was increased to 8,000 psi, solid blocky structures were formed on the surface of the polymer sheet in Sample 8 as shown in FIG 13(a). After removing the silica particles by etching with hydrofluoric acid, a relatively flat surface with fine pore structures were detected. See FIGs. 13(b)-(d). Although these surfaces exhibited hierarchical structures with a sub-micron scale roughness, they did not exhibit superhydrophobicity. As shown in Table 3, the water contact angles of the surface of the polymer sheets in Samples 8 and 9 were lower than 150° and water droplets could not readily slip off the surfaces of these two samples.

The above characterization study demonstrated that the percolative infiltration of polymer into porous nanoparticles can produce superhydrophobic surfaces by creating a multi-level, hierarchical roughness layer on the surface of the polymer. Without wishing to be bound by theory, the levels of roughness could arise from the nanoparticles and nanoparticle agglomerates (e.g., having a length scale of 20-200 nm) to nanoparticle coated polymer filaments formed during the percolative infiltration process (e.g., having a length scale of 1-10 microns) and polymer micro-textures (micro-moguls) formed during relaxation and recrystallization of the polymer substrate (e.g., having a size about 100 microns). Moreover, the process conditions could have a significant effect upon the microstructure and thus the wetting properties of the surface.

Example 3: Dynamic water pressure resistance test

A superhydrophobic polymer sheet was prepared using low density polyethylene (approximately 10 layers where each layer was 0.005" thick). The polymer sheet was placed on a steel plate and put into a press. The polymer sheet was then heated at 123°C under a pressure of approximately 30 psi to form a polymer sheet approximately 1 mm thick. This polymer sheet was subsequently cooled. A layer of silane treated silica nanoparticles (Cabot TS-530) was placed on a piece of paper to make a uniform layer approximately 100 microns thick. The particle coated paper was placed on a lower steel plate. After the 1 mm polymer sheet was placed on the particles, an upper steel plate was placed on top of the polymer sheet. The entire stack-up was placed into a press and heated at 123°C at ~30 psi for ~20 minutes. The press was then opened and the sample was allowed to cool to room temperature.

Water droplets (5 mm diameter) were released from a height of 8.5 meters onto a free-standing superhydrophobic film and the impact was recorded using a Phantom high speed camera from Vision Research at a frame rate of 20,000 frames/second. Impact velocity was estimated at 8.8 m/second based on the height and by tracking the droplet within individual video frames. The drop hit the surface, spread significantly then broke apart into numerous smaller droplets. The surface was not wetted by the drop and remained superhydrophobic after multiple impacts. In addition, pumping water onto the surface at a rate of 100 gallons/hour for 45 hours did not significantly degrade the surface properties. Similarly, the superhydrophobic properties were retained when the polymer sheets were ultrasonicated for 30 minutes in water.

Example 4: Test of a superhydrophobic surface against super-cooled water droplets

Silica nanoparticles (Cabot TS-530) were dispersed in a solution of methanol and stirred. The solution was then dried at 150°C and the particles were placed in the bottom of a steel plate with sidewalls to retain the particles. The thickness of this layer was approximately 3 mm. After a HDPE sheet having a thickness of approximately 0.01 inch was placed on the particles, a flat steel plate was placed on top of the polymer sheet. The stack-up was then laminated at 138°C at a pressure of 300 psi for 30 minutes. The sample was removed from the press and allowed to cool to room temperature. The polymer was then removed from the nanoparticle layer and washed to remove any excess or loose particles.

The ability of the superhydrophobic surfaces of the polymer sheet described above to repel super-cooled water droplets was demonstrated using liquid water droplets 13 μL in volume (3 mm in diameter) cooled to -5.1°C. A portion of the polymer sheet having a superhydrophobic surface prepared above was mounted onto a sloped aluminum block at a 20° angle relative to a horizontal surface. The temperature of the surface was controlled with a closed-loop refrigeration system capable of cooling the aluminum block to a temperature as low as -70°C. Deionized water in a 10cc syringe with a stainless steel syringe tip was cooled to -5.1°C using a Neslab chiller and kept at that temperature for 1 hour before use. Once the surface of the aluminum block was cooled to an appropriate temperature, the syringe was removed from the chiller, mounted at a location 11 cm above the surface, and the super-cooled droplets were allow to impinge upon the cooled surface. When the surface was cooled to temperatures as low as -32°C, a supercooled droplet would bounce off the surface without forming ice. By contrast, when an unprocessed polyethylene sheet was used, the super-cooled droplets froze onto the surface and ice began to accrete immediately after the droplet impinged on the surface.

The experimental results showed that the ability of a superhydrophobic surface to mitigate ice accumulation depended upon the temperature of the surface. Specifically, when the superhydrophobic surface was cooled to temperatures above -13°C, all super-cooled droplets were repelled and no ice was formed on the surface. At lower surface temperatures, however, ice began to accumulate after a certain number of droplets impacted the surface. When the surface was maintained at -32°C, the first 5 drops could bounce off the surface before ice began to accumulate. Below -40°C, all super-cooled droplets froze upon impact. In addition, the results showed that the icephobic properties of a superhydrophobic surface also depended upon droplet size. Ice formation began at higher temperatures when 50 μL (about 5mm diameter) droplets were used. Since the average super-cooled water droplet in the atmosphere is below 0.5 mm, ice accumulation is not expected to occur if the surfaces are maintained at normal atmospheric temperatures (e.g., above -32°C). At these temperatures, superhydrophobic surfaces described herein would be especially resistant to ice accumulation.

Example 5: Test of a superhydrophobic surface against ice accumulation

A superhydrophobic polymer film was made by laminating LDPE against a layer of nanoparticles (TS530) with a thickness of about 100 µm at 123°C under a pressure of about 30 psi for 1 hour using the same process described in Example 3 except that a metal mat is placed between the lower plate of the press and the steel plate supporting the sheet of nanoparticles. The mat was used to distribute the pressure more uniformly, as is commonly done in plate lamination processing. A longer heating time was used as the mat impedes the conduction of heat from the plate to the polymer sheet.

To test the icephobic properties of the superhydrophobic polymer film described above when exposed to small super-cooled liquid water droplets of average size (5-40 µm), the free-standing polymer film was placed on the windshield of a parked car overnight during an ice storm with its superhydrophobic surface exposing to air. Ice accumulated on all exposed surface of the windshield that was not covered by the polymer film. Although some ice did coat a portion of the polymer film, especially the edges, the central portion of the film remained ice-free. By contrast, a film made from untreated polyethylene that was also placed on the windshield was difficult to see as it became encrusted in ice.

Example 6: Fabricating polymer sheets having a superhydrophobic surface by using a template coated with a porous nanoparticle layer

In this example, a template was coated with dry particles before a polymer sheet was laid atop the template. A commercially available thermoplastic sheet of low density polyethylene (LDPE) manufactured by Berry Plastics (Evansville, IN) and sold through McMaster-Carr was used as the polymer sheet. The polymer sheet contained 97% recycled polyethylene, 2% calcium carbonate and 1% slip oleamide. A nylon mesh with a pore diameter of 40 µm and a wire width of 40 µm was coated with silane treated nanoparticles (TS530, Cabot Corporation). During the coating treatment, the pores of templates were partially filled with the nanoparticles. The lamination of the polymer sheet with the template coated with nanoparticles was conducted at 123°C under a pressure of 200 psi for 20 minutes. The cooling and peeling steps were the same as the procedures in Example 1.

The nanoparticles coated on the template generated rough nanostructures on the polymer posts after lamination resulting in surfaces which exhibited improved superhydrophobic properties, such as increased stability towards impinging water droplets compared to samples made in Example 1. By incorporating the nanoparticles, the static water contact angle of the fabricated surface increased from 160° to 165° and the slip-off angle of water droplets decreased down to 3°. Without wishing to be bound by theory, it is believed that surfaces prepared from nanoparticle-coated templates have three levels of roughness. Two roughness levels are similar to those surfaces made in Example 1, albeit less well defined, and correspond to the pores in the template and the filaments used to weave the template. A third level of nano-roughness is added upon these features from the nanoparticles. The nanoparticles were either incorporated into the polymer surface, or create grooves into the surface during the lamination-peel process.

Quantitative testing demonstrated that the superhydrophobicity of the surface prepared above remained unchanged after washing numerous times with a saturated soap solution made with a soap powder (ALCONOX - Powdered Precision Cleaner, from VWR International, containing 7-13% sodium carbonate, 10-30% sodium dodecylbenzenesulfonate, 10-30% tetrasodium pyrophosphate, and 10-30% sodium phosphate) or ultrasonication in the same solution for 5 hours. The results showed that the superhydrophobicity of the fabricated surface possessed good stability under high water pressures. Static pressure tests demonstrated that the superhydrophobic surface remained dry even under a water pressure of 8 psi (5.6 m water) for more than 5 hours, showing a significantly greater water pressure resistance than that of a lotus leaf.

<u>Example 7</u>: Fabricating polymer sheets having a superhydrophobic surface by using a template coated with a porous nanoparticle layer and a polymer sheet coated with a layer of porous nanoparticle layer.

The same Ultra-high-molecular-weight polyethylene (UHMWPE, McMaster Carr, Elmhurst, IL) used in Example 2 was used as the polymer sheet. A steel mesh with a pore size of 309 μm and a wire diameter of 114 μm was used as the template. First, a thixotropic solution was prepared by dispersing silane-treated hydrophobic nanoparticles (e.g. TS-530 from Cabot Corporation) into an appropriate solvent (e.g. a mixture of 30 wt% water and 70 wt% methanol). Subsequently, the polymer sheet and the mesh template were coated with the prepared solution and dried at 150°C for 10 minutes. The thickness of the nanoparticles on the polymer sheet was around 150 μm. The coated mesh and the coated polymer sheet were placed between two flat stainless steel plates. The assembly was then laminated at 200°C and under a pressure of 800 psi for 2 hours. During lamination, the polymer melted and infiltrated the pores between nanoparticles coated on the polymer. With reduced viscosity, the polymer penetrated into the pores of the templates, forming micron sized patterns (0.5 to 10 microns) on the surface of the polymer sheet. As the polymer cooled, a micro-textured roughness is formed to which particles strongly adhered.

The fabricated UHMW PE superhydrophobic surface exhibited excellent water repellency. The static water contact angle was higher than 170° and the slip-off angle of 10 μL water droplets was just above 0°. The polymer surface maintained its superhydrophobicity with a water contact angle of 155° after 100,000 abrasion cycles under a pressure of 32 kPa using the mechanized abrasion test described in Example 1. Moreover, the superhydrophobic surface exhibited excellent scratch resistance. Specifically, water droplets maintained a contact angle higher than 160° after the surface was scratched 50 times using a sharp steel nail.

Other embodiments are within the scope of the claims.

WHAT IS CLAIMED IS:

1. A method, comprising:

laminating a polymer sheet having a surface to a template having a textured surface, the surface of the polymer facing the textured surface of the template; and

separating the polymer sheet and the template, thereby converting the surface of the polymer sheet to a hydrophobic surface having a water contact angle of at least about 150°.

2. The method of claim 1, wherein the laminating step comprises disposing the polymer sheet and the template between two plates.

3. The method of claim 2, wherein the lamination step further comprises pressing the two plates to bring the polymer sheet into contact with the template.

4. The method of claim 1, wherein the polymer sheet comprises a polymer having a melting temperature and the laminating step is performed at a temperature above the melting temperature of the polymer.

5. The method of claim 4, wherein the method further comprises cooling the polymer sheet and the template below the melting temperature before separating the polymer sheet and the template.

6. The method of claim 1, wherein the laminating step is performed at a pressure of at least about 0.5 psi.

7. The method of claim 1, wherein the polymer sheet comprises a thermoplastic or thermoset polymer.

8. The method of claim 1, wherein the polymer comprises a polyolefin, a polyacylate, a poly(vinyl chloride), a polystyrene, a poly(tetrafluoroethylene), a polysiloxane, a polycarbonate, or an epoxy polymer.

9. The method of claim 8, wherein the polymer comprises a low density polyethylene, a high density polyethylene, a linear low density polyethylene, or an ultra-high molecular weight polyethylene.

10. The method of claim 1, wherein the polymer sheet has a thickness of from about 25 μm to about 1 cm.

11. The method of claim 1, wherein the polymer sheet further comprises an inorganic material.

12. The method of claim 11, wherein the inorganic material comprises inorganic nanoparticles, inorganic microparticles, particle agglomerates, inorganic fibers, or inorganic nanofibers.

13. The method of claim 1, wherein the template comprises a mesh, a fabric, a porous membrane, or a sandpaper.

14. The method of claim 13, wherein the template comprises a mesh having an average pore size of from about 2 μm to about 800 μm.

15. The method of claim 14, wherein the mesh has an average depth of pores ranging from about 2 μm to about 800 μm.

16. The method of claim 1, wherein the method further comprises disposing inorganic nanoparticles onto the template before the laminating step.

17. The method of claim 16, wherein the inorganic nanoparticles comprises SiO_2 nanoparticles, TiO_2 nanoparticles, Al_2O_3 nanoparticles, or carbon nanoparticles.

18. The method of claim 17, wherein the inorganic nanoparticles have an average diameter of from about 3 nm to about 1000 nm.

19. The method of claim 1, wherein the hydrophobic surface has a water slip-off angle of at most about 5°.

20. The method of claim 1, wherein the hydrophobic surface remains dry under a water pressure of at least about 8 psi for at least about 5 hours.

21. A method, comprising:

laminating a polymer sheet having a surface to a layer of a nanomaterial, thereby converting the surface of the polymer sheet to a hydrophobic surface having a water contact angle of at least about 150°.

22. The method of claim 21, wherein the laminating step is performed by plate lamination, autoclave lamination, or roll lamination.

23. The method of claim 21, wherein the polymer sheet comprising a polymer having a melting temperature and the laminating step comprises heating the polymer at a temperature above the melting temperature of the polymer.

24. The method of claim 21, wherein the laminating step is performed at a pressure of at least about 0.5 psi.

25. The method of claim 21, wherein the polymer sheet comprises a thermoplastic or thermoset polymer.

26. The method of claim 21, wherein the polymer comprises a polyolefin, a polyacrylate, a poly(vinyl chloride), a polystyrene, a poly(tetrafluoroethylene), a polysiloxane, a polycarbonate, or an epoxy polymer.

27. The method of claim 26, wherein the polymer comprises a low density polyethylene, a high density polyethylene, a linear low density polyethylene, or an ultra-high molecular weight polyethylene.

28. The method of claim 21, wherein the polymer sheet has a thickness from about 25 μm to about 1 cm.

29. The method of claim 21, wherein the polymer sheet further comprises an inorganic material.

30. The method of claim 29, wherein the inorganic material comprises inorganic nanoparticles, inorganic microparticles, particle agglomerates, inorganic fibers, or inorganic nanofibers.

31. The method of claim 29, wherein the polymer sheet comprises a layer of inorganic nanoparticles on the surface.

32. The method of claim 31, wherein the layer of inorganic nanoparticles has a thickness of at least about 1 μm.

33. The method of claim 32, wherein the layer of inorganic nanoparticles is porous.

34. The method of claim 21, wherein the layer of the nanomaterial is disposed on a template.

35. The method of claim 34, wherein the template comprises a mesh, a fabric, a porous membrane, or a sandpaper.

36. The method of claim 35, wherein the template comprises a mesh having an average pore size of from about 2 μm to about 800 μm.

37. The method of claim 36, wherein the mesh has an average depth of pores ranging from about 2 μm to about 800 μm.

38. The method of claim 34, wherein the polymer sheet comprises a layer of inorganic nanoparticles on the surface

39. The method of claim 21, wherein the layer of the nanomaterial comprises inorganic nanoparticles.

40. The method of claim 39, wherein the inorganic nanoparticles comprise SiO_2 nanoparticles, TiO_2 nanoparticles, Al_2O_3 nanoparticles, or carbon nanoparticles.

41. The method of claim 39, wherein the inorganic nanoparticles have an average diameter of from about 3 nm to about 1000 nm.

42. The method of claim 21, wherein the hydrophobic surface has a water slip-off angle of at most about 5°.

43. The method of claim 21, wherein the hydrophobic surface remains dry under a static water pressure of 8 psi for about 5 hours.

44. The method of claim 21, wherein the hydrophobic surface has a water contact angle of at least about 150° after 1000 abrasion cycles under a pressure of 32 KPa.

45. The method of claim 21, wherein the hydrophobic surface has a water contact angle of at least about 150° after the hydrophobic surface is scratched by a steel nail 10 times.

46. An article, comprising:

a polymer sheet having a hydrophobic surface, the hydrophobic surface having a water contact angle of at least about 150° and having a plurality of protrusions;

wherein the plurality of protrusions has an average length or width of from 2 μm to about 500 μm.

47. The article of claim 46, wherein the plurality of protrusions has an average height of from about 25 μm to about 1000 μm.

48. The article of claim 46, wherein the plurality of protrusions has an average distance of from about 5 μm to about 500 μm between two neighboring protrusions.

49. An article, comprising:

a polymer sheet having a hydrophobic surface, the hydrophobic surface having a water contact angle of at least about 150°; and

a plurality of nanoparticles disposed on the hydrophobic surface, at least some of the nanoparticles being partially embedded in the polymer sheet and partially exposed on the hydrophobic surface.

50. The article of claim 49, wherein the polymer sheet comprises a plurality of protrusions on the hydrophobic surface, each protrusion having a top surface and a side wall.

51. The article of claim 50, wherein at least some of the nanoparticles are disposed on the top surface and the side wall of each protrusion.

52. The article of claim 51, wherein the polymer sheet has a surface between two neighboring protrusions and at least some of the nanoparticles are disposed on the surface between two neighboring protrusions.

53. The article of claim 52, wherein the surface between two neighboring protrusions and the top surface of a protrusion have an average distance of from about 2 μm to about 800 μm.

54. The article of claim 49, wherein the polymer sheet comprises a plurality of protrusions on the hydrophobic surface, the protrusions having an average length or width of from 0.5 μm to about 10 μm.

55. An article, comprising:

a polymer sheet having a hydrophobic surface, the hydrophobic surface having a water contact angle of at least about 150° after 1000 abrasion cycles under a pressure of 32 KPa.

56. The article of claim 55, wherein the hydrophobic surface has a water contact angle of at least about 150° after the hydrophobic surface is scratched by a steel nail 10 times.

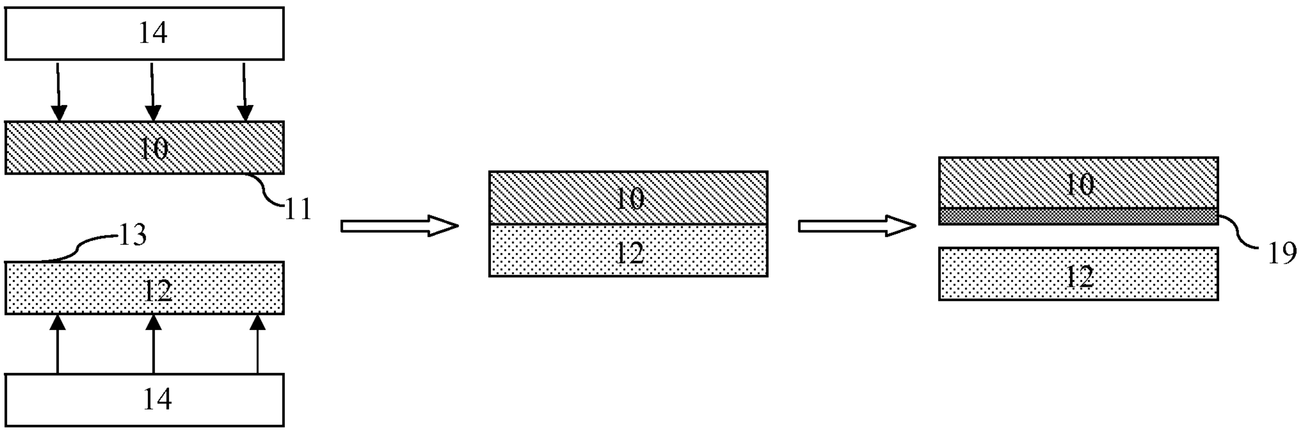

FIG. 1

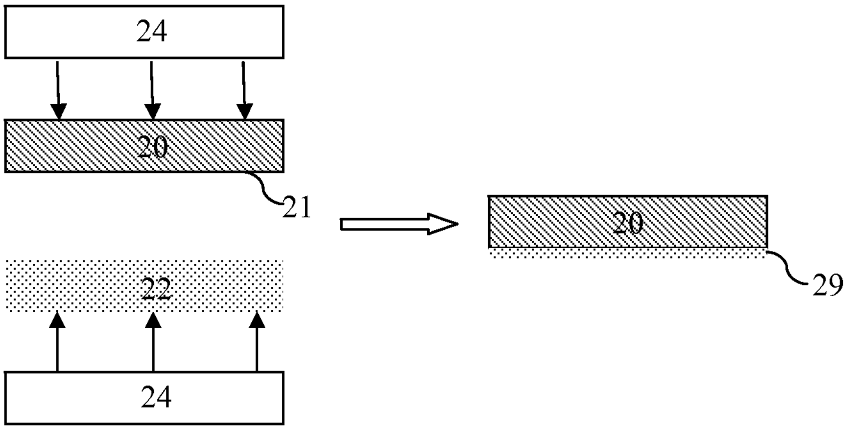

FIG. 2

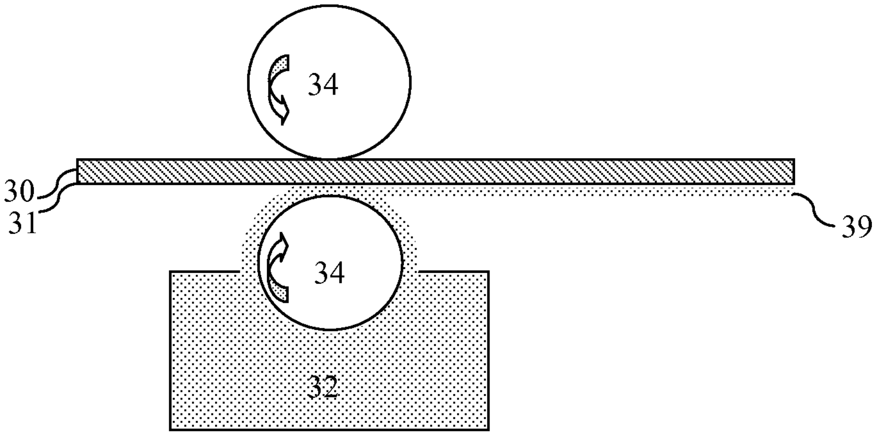

FIG. 3(a)

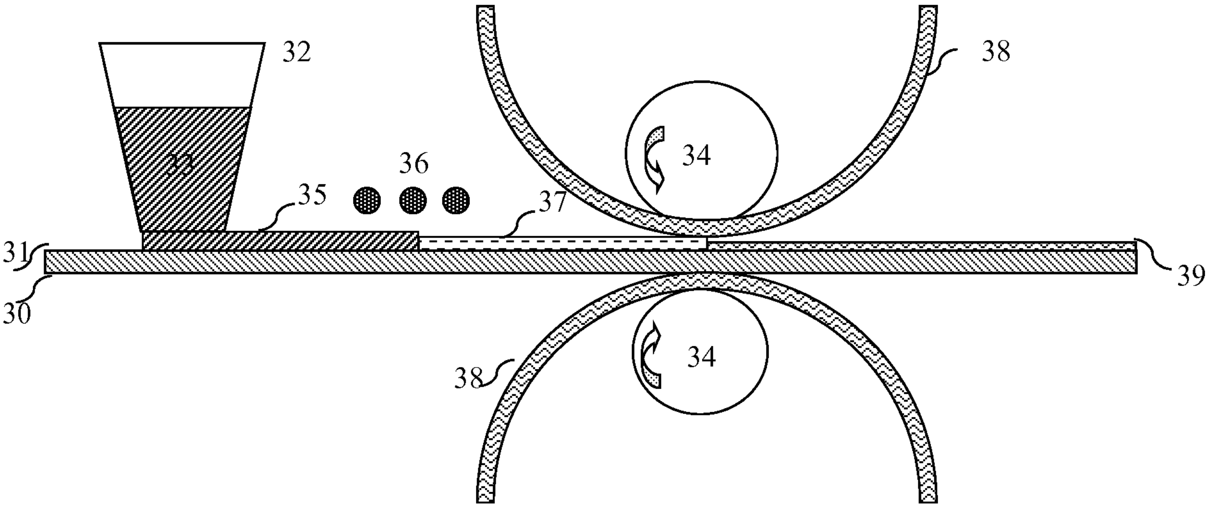

FIG. 3(b)

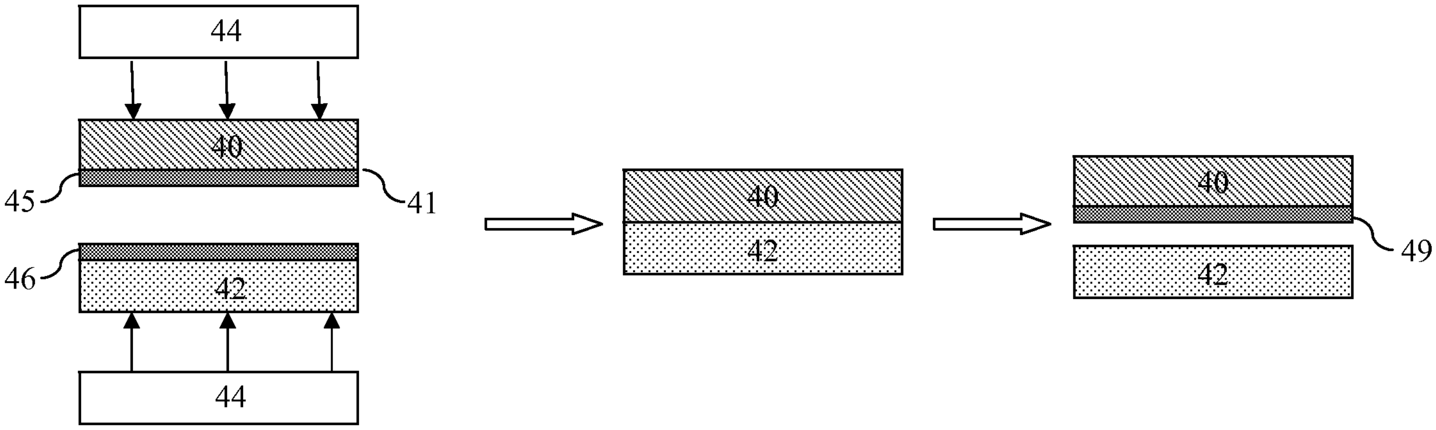

FIG. 4

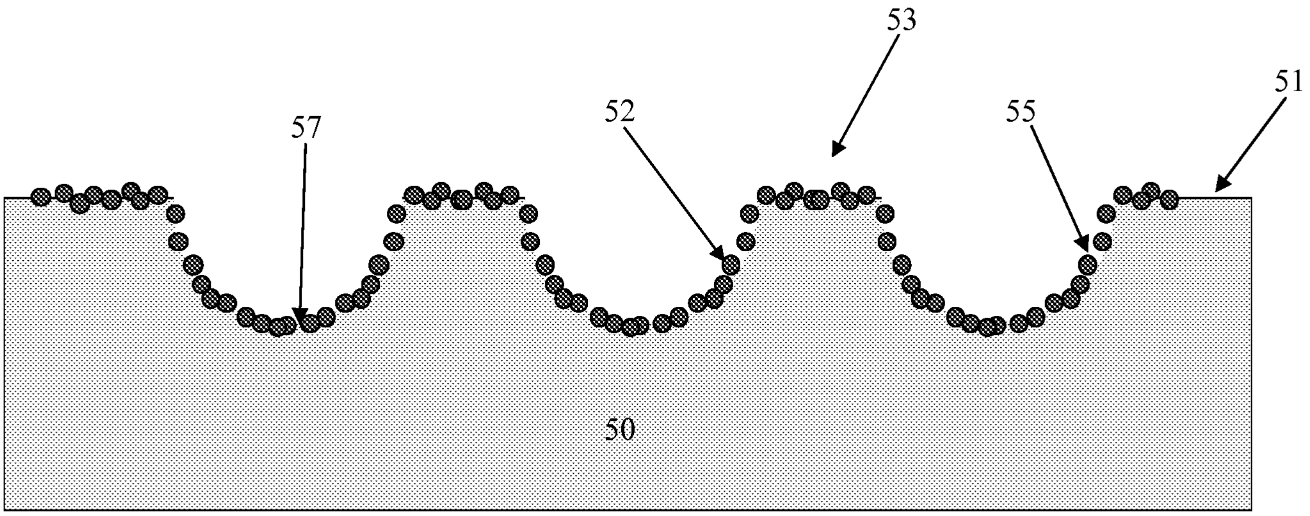

FIG. 5

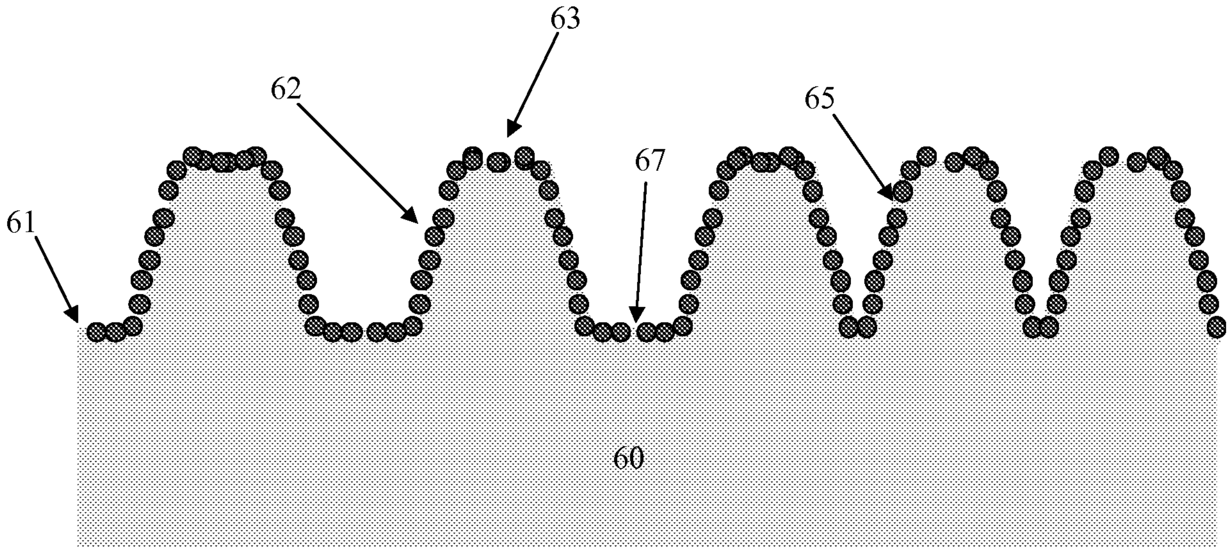

FIG. 6

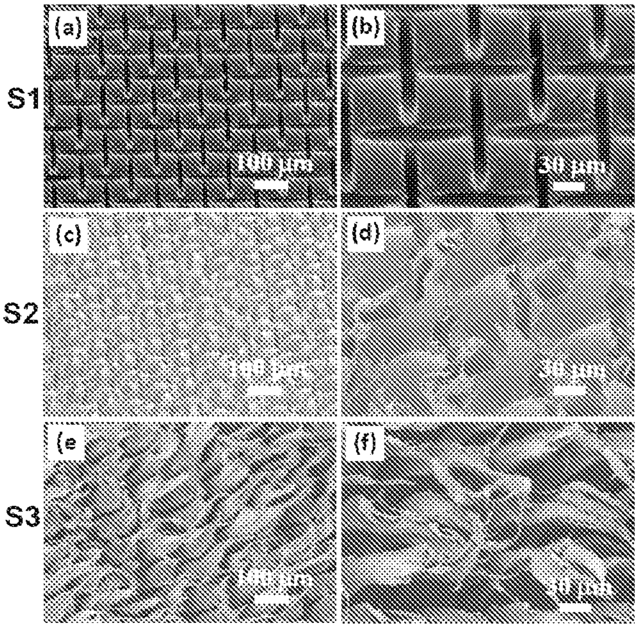
S1
(a)
100 μm
(b)
30 μm
S2
(c)
100 μm
(d)
30 μm
S3
(e
100 μm
(f)
30 μm

FIG. 7

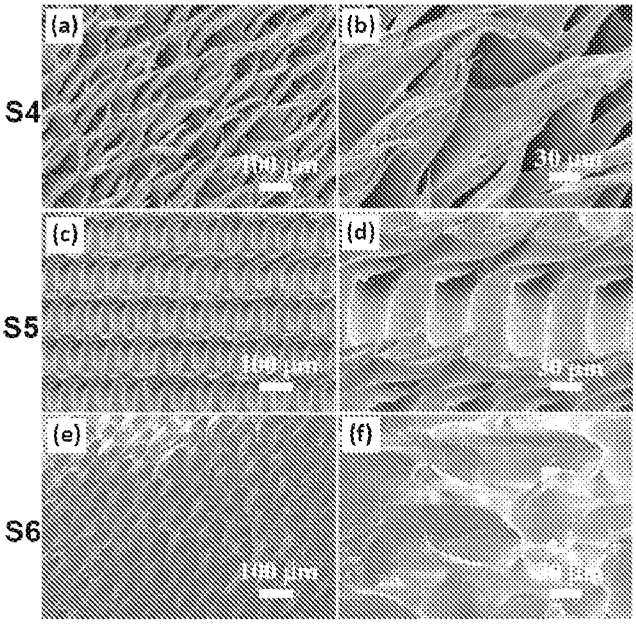
S4
(a)
100 μm
(b)
30 μm
S5
(c)
100 μm
(d)
30 μm
S6
(e)
100 μm
(f)

FIG. 8

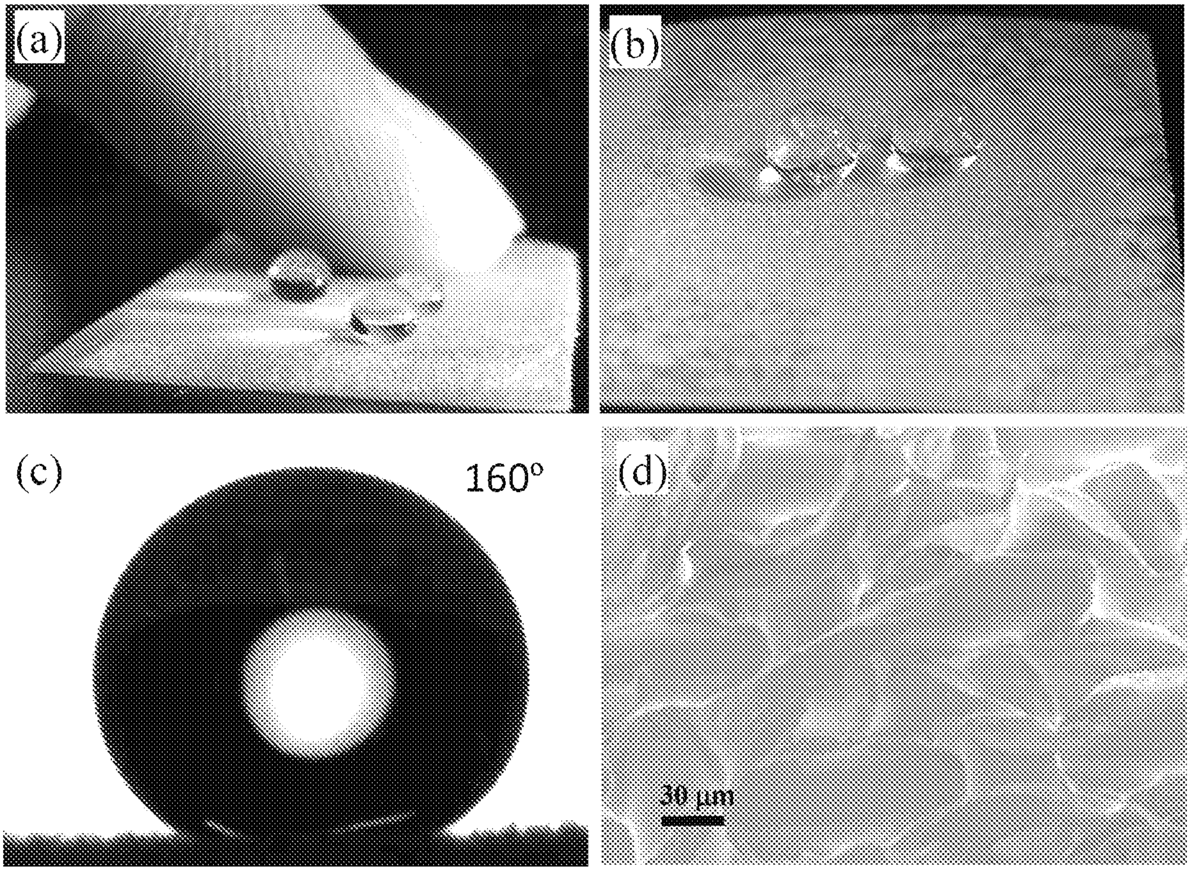

FIG. 9

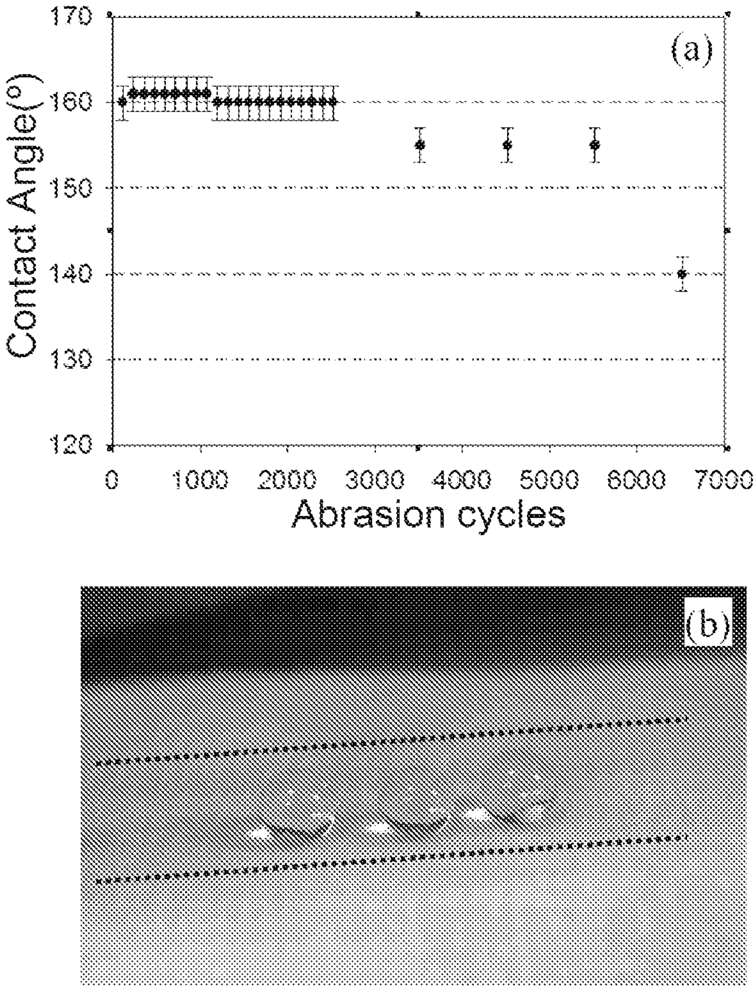
(a)
Contact Angle(°)
170
160
150
140
130
120
0
1000
2000
3000
4000
5000
6000
7000
Abrasion cycles
(b)

FIG. 10

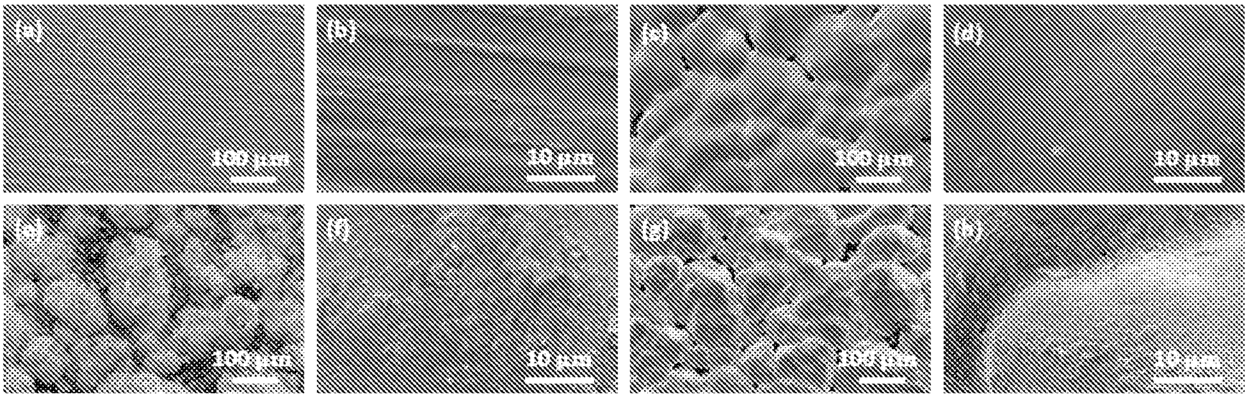
(a)
100 μm
(b)
10 μm
(c)
100 μm
(d)
10 μm
(e)
100 μm
(f)
10 μm
(g)
100 μm
(h)
10 μm

FIG. 11

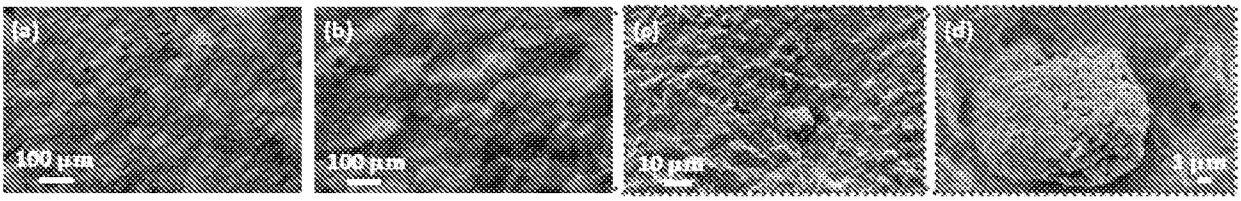
(a)
100 μm
(b)
100 μm
(c)
10 μm
(d)
1 μm

FIG. 12

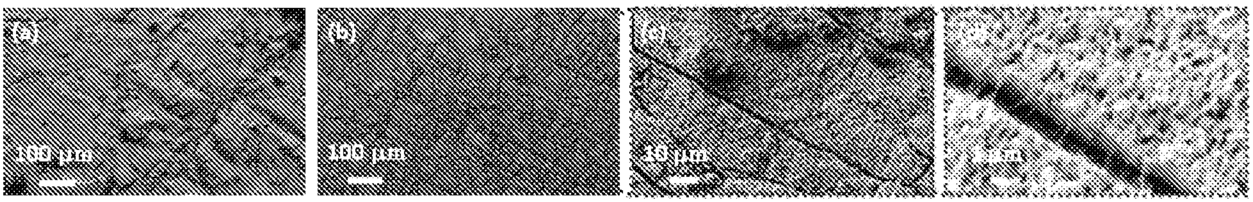

FIG. 13