A simple fabrication route to a highly transparent super-hydrophobic surface with a poly(dimethylsiloxane) coated flexible mold

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A super-hydrophobic and highly transparent nanostructured film was fabricated *via* imprinting and conformally uniform chemical anchoring of poly(dimethylsiloxane) on a controlled nanoscopic dimension.

Many researchers have focused on fabricating super-hydrophobic surfaces, which are potentially suitable for various applications, such as dust-free and self-cleaning surfaces for solar cells, satellite dishes, roofing and building glasses.[1,2] The wettability of surfaces is governed by both their chemical modifications and geometrical structures.[3–5] The flat surface covered by aligned closest hexagonal packed $-CF_3$ groups, which has the theoretically highest water contact angle and lowest surface energy, has been shown to have a water contact angle up to 120°.[3] In nature, however, various super-hydrophobic surfaces such as lotus leaves, cicada wings and rice leaves, which have small and fractal structures on their surfaces, have been found to have water contact angles greater than 120°.[6–8] As super-hydrophobicity has been influenced by both the surface energy of the coating materials and surface roughness,[5–16] surface structures are also important in enhancing super-hydrophobicity. For this reason, various fractal micro- and nanostructures, for example, nanotubes, nanofibers, nanofilaments, nanopins, nanorods, colloidal microstructures, honeycomb-like membranes and inorganic fractal surfaces such as TiO_2, have been introduced as super-hydrophobic surface structures.[6,7,9–15]

For various optical applications whose dust-free and self-cleaning surfaces are attributed to super-hydrophobicity, the transparency and clearness of the film with the super-hydrophobic surface is also an important property.[10,14–16] Generally, surface roughness and transparency are competitive properties. When surface roughness increases, the hydrophobicity increases, whereas the transparency decreases. The blur of surface roughness is mainly induced by Mie scattering effects,[17] which are dominantly effective on structures that are comparable in size to the visible light wavelength. However, structures with dimensions below 100 nm on a film make the film more transparent, rather than blurred by Mie scattering,[14,16,17] when its nanostructured surface shows a refractive index change between air and substrate due to the nanostructure.[18] Anti-reflective coatings reduce the intensity of reflection and increase the quality of an optical film. For anti-reflective coatings, the reflective index of the film is reduced ideally to 1.22. But, a homogeneous layer cannot obtain this value; therefore, nanoporous structures or embossed nanostructures are used for anti-reflective coatings.[19]

Many optical polymer films, including polarized film and prism sheets, are in use. With the transparencies of optical polymer films being similar to that of glass, and boosted by a low cost, various processes for optical applications using polymer films have been developed. Nanoimprint techniques with a flexible mold are useful for the surface-texturing of polymer films since polymer structures can be simply fabricated from a replica mold, it is economical and protects the master from contamination during the process.[20,21]

In the present study, we introduce a simple fabrication technique based on nanoimprint lithography using ultraviolet rays (UV) to cure a polymer for a super-hydrophobic coating with high transmittance. For both super-hydrophobicity and anti-reflection, we used a self-assembled nanoporous anodic aluminium oxide (AAO) template as the master pattern which has a uniform-dimension of nanostructures over a range.[22] The alumina membranes with regular pore diameters were fabricated *via* a two-step anodization, employing 0.3 M oxalic acid as an electrolyte with an anodization voltage of 40 V. A more detailed description of the process is given in our previous work.[23]

A thin film of poly(dimethylsiloxane), PDMS,[24] is used as both a super-hydrophobic coating material and as anti-adhesion release layers in nanoimprint lithography because PDMS has a fairly low surface energy and provides easy release between the mold and the patterned polymer on the substrate. Siloxane-based PDMS possesses a critical surface tension of 21 mN m^{-1}, which is similar to that of TFE-based PTFE (24 mN m^{-1}), a commonly used super-hydrophobic layer.[25] In nanoimprint lithography with a flexible mold, the release of molds from the polymer patterns is affected by various factors, such as surface energy, and storage and loss moduli. Although perfluoro-groups have very low surface energy, the adhesion force, represented by the peel fracture energy, of an intrinsic PDMS surface is lower than that of a surface treated with perfluoro-groups.[24,26] On this basis, we used a PDMS layer as both a super-hydrophobic coating and an anti-adhesion release layer.

Scheme 1 shows the fabrication procedure of a PDMS layer coating,[24] which is used as both a super-hydrophobic coating material with high transmittance and an anti-adhesion release layer on the nanostructured mold. Aminosilane grafting on the surface of an AAO nanotemplate or polymer mold was attained by the treatment of the surface of the mold with oxygen plasma and then immersing it in a 0.5 wt% aqueous solution of 3-(aminopropyl)-triethoxysilane (APTES) for 10 min. Following the removal of

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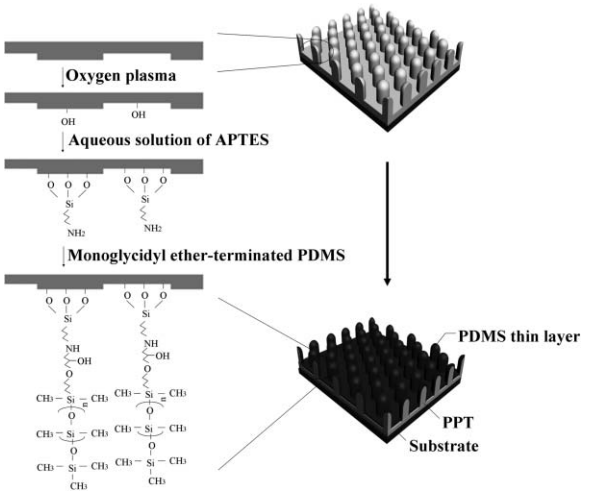
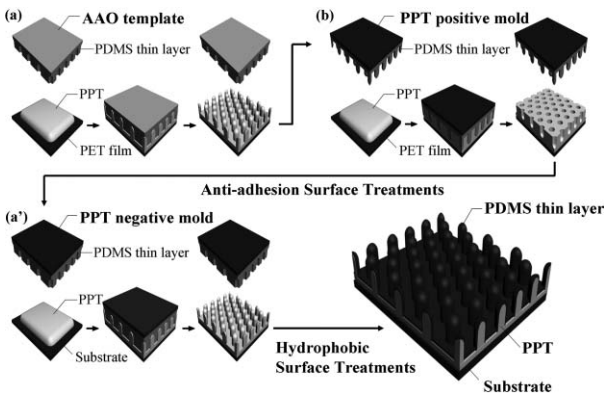


Scheme 1 Schematic illustration of PDMS coating onto the nanopatterned surface.[24]

unreacted APTES by washing with distilled water, monoglycidyl ether-terminated PDMS was added dropwise and the reaction mixture was heated at 80 °C for 4 h. The mold was immersed in 2-propanol and sonicated for 1 min to remove unreacted PDMS. The covalent bonding formed by epoxy–amine chemistry between monoglycidyl ether-terminated PDMS and the aminosilane-treated surface makes it possible to establish the strong and highly stable coating without roughening of the surface.[24,27] Since hydroxyl groups can be easily generated on a surface through oxygen plasma treatment, and the epoxy–amine reaction makes the strong and stable chemical bonding, the thin PDMS layer can be easily formed on virtually any surface.

Scheme 2 shows the fabrication procedure of super-hydrophobic nanostructures on a substrate using polymer molds with ordered nanodot-arrays that are inversely replicated from an AAO template. Molds for various purposes require process flexibility. With anodic alumina templates being too hard and brittle for a master mold in nanoimprint lithography, we fabricated a flexible polymer mold with the same nanostructures as the surface structures of the AAO templates.



Scheme 2 Schematic illustration of the replication of a highly transparent super-hydrophobic surface by nanoimprint lithography with a flexible polymer mold. Illustrations (a), (b), and (a′) represent nanoimprint lithography. For each step, the replica and mold were coated with PDMS (as mentioned in Scheme 1) to obtain an anti-adhesion release layer and hydrophobic surface.

The AAO templates, which are the primary master, were coated with an anti-adhesion PDMS layer for easy release of the polymer mold from the AAO templates, as mentioned in Scheme 1. First, using PDMS-coated AAO templates as a master pattern, the nanoporous structures of the AAO templates were printed on a UV curable pentaerythritol propoxylate triacrylate (PPT) precursor solution on a polyester (PET) flexible film. With PPT being a strongly adherent coating material on an inorganic or organic substrate, we replicated the nanostructures on PPT on a PET film, using the PDMS-coated AAO templates as the master. After curing with UV light ($\lambda \simeq 365$ nm) for 30 min, the PPT replica mold was peeled off (Scheme 2a). Then, the PPT replica mold was coated with a PDMS layer as an anti-adhesion release layer to facilitate easy release of the mold. Using a PDMS-coated PPT replica mold, we printed again on a UV curable PPT precursor solution on a PET film *via* the same procedures as mentioned above. This PPT negative mold had the same pattern as the original AAO templates (Scheme 2b).

The PPT negative mold was, once again, coated with an anti-adhesion PDMS thin layer for easy release, and was used to fabricate a PPT positive mold on a PET film or glass substrate (Scheme 2a′). Finally, the above PPT positive mold was coated with a PDMS thin layer in order to make its surface hydrophobic. Since this PPT positive replica contains nanodots, and is inversely replicated from AAO templates that have the very low surface energy of PDMS, this PPT replica on a flexible PET film or glass substrate shows good super-hydrophobic properties.

Fig. 1 shows the tilted SEM images of the AAO templates (Fig. 1a) and the final replica (Fig. 1b), which were coated with a PDMS thin layer. The insets are magnified images of the top-view. When fabricating transparent super-hydrophobic films, roughness on the mold should be controlled. The pore size of the AAO templates used was ~57 nm with a depth of ~100 nm. To induce hydrophobicity and easy release, we coated a PDMS layer onto the surfaces of both the AAO templates and polymer replicas. The thickness of the PDMS thin layer coated on the protruding surface of the nanostructures on the mold was very thin (< ~10 nm),[24] which indicates that the replica is nearly unaffected by the binding of the PDMS layer. The PPT replica (Fig. 1b) shows a typical morphology for a super-hydrophobic surface.

The water contact angle was measured by sessile drop fitting. A sessile drop is a sitting drop, as in a drop of water resting on a table. The contact angle measures the relationship between a liquid and the surface characteristics of a solid on which the liquid is placed. In the case of the final replica, which was coated with a

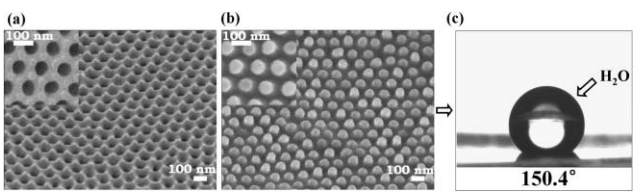


Fig. 1 SEM images of the anodic alumina templates and final replica: (a) AAO templates (pore size ~57 nm, depth ~100 nm); (b) the final PPT replica for the highly transparent super-hydrophobic film, fabricated using nanoimprint lithography with the flexible mold that had the same pattern as the AAO templates. (c) The water contact angle of the final PPT replica coated with a PDMS thin layer.

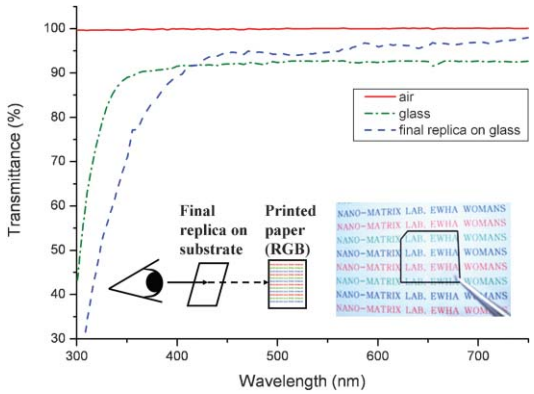


Fig. 2 The transmittance of the highly transparent super-hydrophobic surface and a photograph of letters underneath the transparent super-hydrophobic film.

PDMS thin layer, the contact angle was measured to be 150.4° (Fig. 1c). This result shows that this replication process is good enough to endow super-hydrophobicity onto various substrates.

Fig. 2 represents the transmittance spectrum in the visible region for the third replicated film after the PDMS layer coating. The transmittance of the super-hydrophobic film (PPT replica) on glass and references (air and bare glass) were measured using a UV-vis spectrophotometer. The transmittance obtained for the super-hydrophobic film was higher than that of glass in the visible wavelength range. For the transparency of the films, the surface nanostructures should be controlled below 100 nm,[14,16,17] since structures on the films that are comparable in size to the visible light wavelength are not transparent due to Mie scattering. Owing to anti-reflective effects, which were attributed to the embossed nanostructures on the glass substrate, this film on glass shows a higher transmittance than bare glass, an average of ~95%, for the wavelength range from 430 nm to 750 nm. Anti-reflective coatings reduce the intensity of reflection and increase the quality of the optical film. These properties of the nanostructure surface, as well as the super-hydrophobicity, are useful for various optical applications. As can be seen in the inset of Fig. 2, letters underneath the film were not blurred, and the RGB colors were clearly legible.

In summary, we have demonstrated the highly transparent super-hydrophobic surface fabrication strategy using nanoimprint lithography with a flexible mold. Also, we have presented the PDMS-based coating strategy to achieve both a highly transparent super-hydrophobic surface and an anti-adhesion layer coating for high-resolution nanoimprint lithography by intrinsic low surface energy and easy release of PDMS. The PDMS-coated flexible mold was used repeatedly, more than 10 times, without losing the anti-adhesion property of PDMS and endured severe chemical cleaning processes, such as sonication, which were performed periodically to wash the mold after several consecutive imprintings. Our approaches are very suitable for various applications that require both super-hydrophobic and anti-reflective surface coatings. This strategy can be easily extended to a large area patterning; therefore, this simple and cost-effective method is good for the mass production of nanopatterned polymeric optical substrates, and is applicable to such cases as solar cell applications and plastic optics which require dust-free and self-cleaning surfaces with high transmission.

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