Manipulation of surface properties: the use of nanomembrane as a nanometer-thick decal

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1. Fabrication of free-standing nanomembrane

The general procedure of the nanomembrane fabrication is as follows (Fig. S1). A sacrificial layer is first formed on a flat silicon wafer by spin-coating. Poly(styrene-4-sulfonic acid) [PSS] and poly(4-hydroxystyrene) [PHS] were usually used as water-soluble and ethanol-soluble sacrificial layers, respectively. Then, a thin layer of nanomembrane precursor is additionally formed with thickness of several tens of nanometer. The double layer is cured by heating on a digital hot plate when thermosetting resin was used as the nanomembrane. Adequate photo-irradiation was done for photopolymers and inorganic/organic hybrid. And it is detached from Si wafer by dissolution of the sacrificial layer. The detached nanomembrane was attached to a wire frame by careful scooping to express free-standing self-supporting ability.

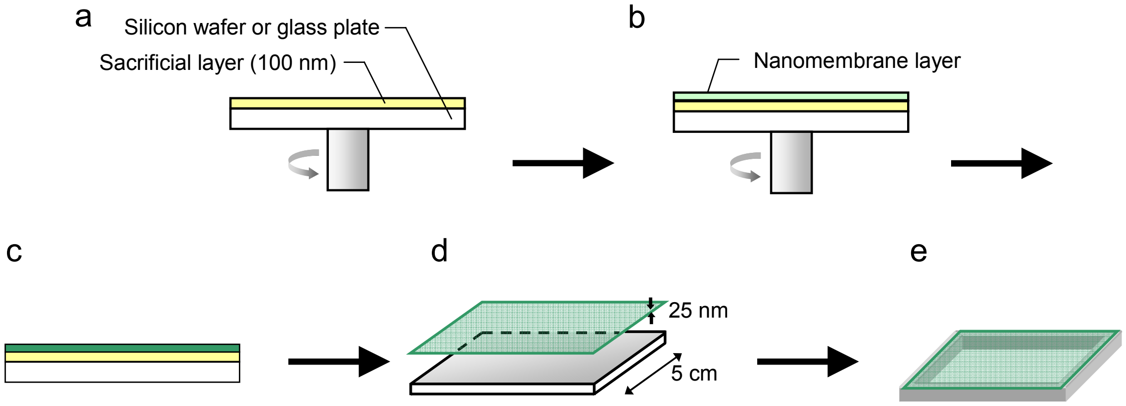

Fig. S1. General preparative procedure of nanomembrane. a, Spin-coating of underlayer. b, spin-coating of nanomembrane precursors. c, cross-linking by photo-irradiation or heating. d, recovery into/onto solvent by dissolution of sacrificial layer. e, expression of free-standing ability in air.

2. Physical properties of directly-fabricated film

As confirmed by SEM observations, regular pillar patterns were clearly observed on the surface of a nano-imprinted NIAC23 polymer film that was directly fabricated onto a Si substrate. Total film thickness can be adjusted from several hundred nanometer to micron order by the change in original film thickness. On the other hand, the height of the pillars remained constant at 200 nm because the pillars were obtained as replicas of the mold, which has hole-patterns of 200 nm depth. Although AFM measurements are useful a tool to evaluate the replicability of nano-imprinting, precise height profiles were not obtained due to the limitation of the AFM cantilever size.

IR and QCM measurements have conveniently been used to monitor a nanometer-thick assembly on flat surfaces, but they are not suitable for directly following the current nano-coating on patterned surfaces. Thus, we separately confirmed the growth of a fluorinated layer on a flat surface under similar conditions. A NIAC23 thin film was directly fabricated onto Au-coated glass, and the reflection FT-IR spectrum was measured before and after nano-coating. An absorption peak at 1,254 cm^{-1}, which originates from symmetric stretching vibration of the C-F group was clearly observed after nano-coating, and the differential spectrum was in good agreement with that of Durasurf-DS5100 itself (Fig. S2). This suggests that fluorinated layer was successfully formed on the surface. Subsequently, QCM measurement was performed on a sample that was directly formed onto a QCM gold electrode. A frequency decrease of 420 Hz was observed after nano-coating, and the corresponding fluorinated layer thickness was estimated as 2.7 nm. We assumed that nano-coating was performed with a uniform thickness even on the surface of our patterned samples.

The wettability of these directly-fabricated samples was evaluated by static CA measurements. Static CA for water was 54.3° on a flat surface, and the value was enhanced on a nano-imprinted surface with pillar patterns. Nano-coating also increased the apparent CA. The highest CA of 142.7° was obtained as the result of the combination of these two methods. It should be noted that the calculated value of the area fraction of the pillar using the Cassie-Baxter equation[S1] is in good agreement with the value obtained by SEM observation. CA data of the nano-coated samples with and without nano-imprinting were used in the calculation. Area fractions were obtained as 0.26 and 0.29 for a calculated value from CA data and the direct value by SEM observation, respectively. As the NIAC23 polymer without nano-coating was slightly swollen by liquid droplets, detailed analysis of the other case is impossible. The CA for CH_2I_2 decreased on a nano-imprinted surface. This can be roughly explained by the difference in wetting mode. A CH_2I_2 droplet fully filled the grooves of the patterned texture, and provides for the decrease in CA compared with a flat surface[S2].

References to Supplementary Information

S1 A. B. D. Cassie, *Trans. Faraday Soc.,* **1944**, 40, 546-551.
S2 R. N. Wenzel, *Ind. Eng. Chem.,* **1936**, 28, 988-994.

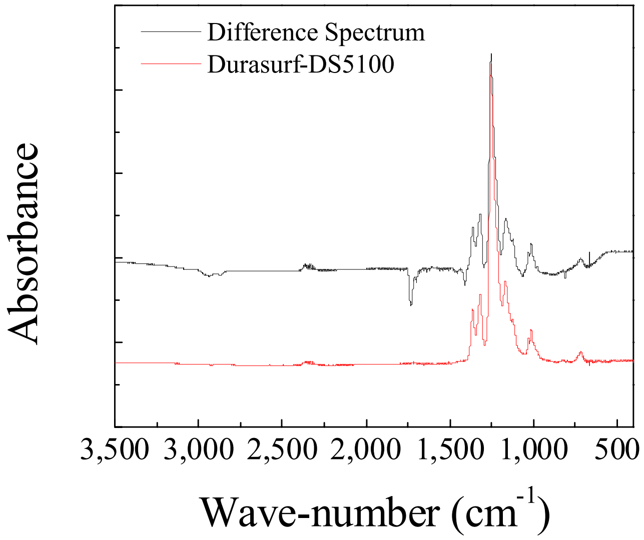

Fig. S2. Reflection FT-IR spectrum of films. Differential spectrum before and after nano-coating with Durasurf-DS5100 (black line), and reflection spectrum of Durasurf-DS5100 thin layer which was directly fabricated on Au substrate (red line).