Electronic Supplementary Material (ESI) for Soft Matter. This journal is © The Royal Society of Chemistry 2016

Supporting Information

Fabrication process:

The non-lithographic fabrication process was started with a four inch aluminum wafer 6061 from OnlineMetals USA. Wet etching process was used to produce nanostructures on aluminum wafer. 75 min etching was done in a 1M HCl solution prepared from 37% HCl Sigma Aldrich. After 2 min carefully rinsing the wafer with diluted water and nitrogen gun drying, 25 nm thick TiO_2 was deposited on it using ALD. Shortly, titanium oxide (TiO_2) 25 nm ± 1% thick at 300°C temperature was grown in a Beneq TFS-500 reactor using titanium chloride $(TiCl_4)$ as a metal precursor and water as a precursor for oxidation. The pressure in the reactor was kept at about 4 Torr. Nitrogen was used as a carrier gas and to purge reaction gases from the reactor during each reaction half cycle. 400 cycles of 1500 ms precursor pulses and 1500 ms purge pulses (the same for both precursors) were used. Long purge and pulse time is needed for fully cover the 3D high aspect ratio nanostructures of template. Then a five millimetre thick PDMS layer (10:1) was cured at 50°C on top of aluminum/titania sample. Finally, the aluminum wafer was sacrificially etched in a 10M HCl solution. This resulted transferring the titania layer to the PDSM surface. The hybrid of PDMS/titania was dried in an oven at 50°C for one hour.

Other templates:

To show versatility of the method, other than aluminum 6061 wafer, we used different complicated hierarchically structured masters for replication. In case of aluminum we produced different hierarchical structures depending on details of the etching process. **Figure S1** shows the SEM of etched aluminum foil (Fig. S1a) in 1M HCl etchant, aluminum wafer 6061 etched in 1M HCl etchant (Fig. S1b), aluminum wafer 6061 etched in 6M HCl etchant (Fig. S1c), and their replicas using ALD film (Fig. S1d-f). The XPS data depicted on **Figure S2** confirms the existence of titania on PDMS after replication.

Robustness Study:

Figure S3 shows a set of studies conducted to study the robustness of superhydrophobicity of our hybrid materials. A sharp knife (Fig. S3a) was used to make 10 perpendicular cuts on the surface. A water droplet rolled off from the surface without pinning after scratches. This is due to a thick porous area that keeps the surface superhydrophobic even after mechanical damage. To show the elastomeric properties of the hybrid material, we bend the surface convex up and down (Fig. S3b) for 100 times and then measure the water contact angle and no difference on contact angle was noticed. Scotch tape test (Fig. S3c) has done for 10 times to show the good adhesion of titania to PDMS. The samples were subjected to a water jet with velocity of 5±2 m/s for one minute (Fig. S3d) without losing the superhydrophobicity. To simulate rain drops, we used droplets falling to the surface from a 3 m height (Fig. S3e) and droplets were bounced off from the surface shows robust superhydrophobicity. By rubbing the sample with bare finger while pushing it (Fig. S3f), we showed the samples are not contaminated by the oil of human finger. Figure S3g shows self-cleaning properties even after bare finger rubbing experiment. Water dipping is one of the most critical studies for superhydrophobic surfaces. Usually water can eventually penetrate through the surface structures to wet the surface. But due to thick and hierarchical re-entrant structures in our samples, the surface remained superhydrophobic even after 90 days in the water (Fig. S3h). Although micro-size air pockets were disappeared after 20 days (Fig. S3i), nano-size air pockets (Fig. S3j) remained in place and kept the surface superhydrophobic. Figure S4a-c shows the SEM images of PDMS/titania samples after 6 hours HF, HCl and KOH treatment respectively.



Figure S1. SEM micrograph of differently etched aluminum templates and their replicas, a) Aluminum foil etched in 1M HCl, b) Aluminum wafer 6061 etched in 1M HCl, c) Aluminum wafer 6061 etched in 6M HCl. All templates are coated with 25nm ALD TiO₂. d-f) Replicated PDMS/titania form the template a-c respectively. Scale bars in (a) and (d) are 10 μ m, for rest are 2 μ m.



Figure S2. XPS data of the PDMS/titania sample after replication confirms the existence of titania.





Figure S3. Robustness study of superhydrophobicity, a) Knife scratching, b) bending, c) scotch tape test, d) water jet, e) drop fall from 3 m height, f) rubbing while pushing with bare finger. g) Self-cleaning properties after 10 times rubbing with bare finger, water droplet is rolling off from the inclined sample and removing the dirt from the surface. h) Storage under DI water, transition from (i) micro to (j) nano-Cassie state happened after day 20th and water contact angle stabilized at 157° for next 70 days.



Figure S4. SEM micrographs of PDMS/titania samples 6 hours immersed in, a) HF, b) HCL, c) KOH. Titania film remained intact in HF and HCl but started to get etched in KOH.