

Supporting information: Fabrication of superhydrophobic surfaces for applications in total internal reflection effects

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1. Silicon nanopillar fabrication

1.1. Preparation of monodisperse PS spheres

Monodispersed PS nanoparticles were prepared by a dispersion polymerization method with DI water and ethanol (99.6%) as a dispersion medium, potassium persulfate (KPS) ($\leq 99.0\%$) as initiator, sodium dodecyl sulfate (SDS) ($\leq 99.5\%$) as emulsifier and styrene as a monomer (99.8%) [1]. Firstly, we used 7 ml of a solution containing ethanol and DI water with a ratio of 5:2 to dissolve 0.011 g of SDS, following magnetic stirring at 70°C with a rate of 800 rpm for 15-20 min. Then, 0.7 ml of styrene and 0.01 g KPS were added to this solution. The amount of styrene decides the size of PS nanoparticles. Here, we provided the amount of styrene for growing 800 nm diameter PS nanoparticles. The solution was kept stirring for more 8 h for polymerizing. The obtained PS solution was washed with ethanol in ultrasonic agitation to remove soluble impurities, followed by a filtration step of PS nanoparticles.

1.2. Fabrication of self-organized hexagonal closed-pack

Angled interface coating, also known as Langmuir-Blodgett coating, was used to fabricate a self-organized hexagonal closed pack of PS nanospheres on silicon substrates. Firstly, a solution containing 10% PS nanoparticles in DI water and ethanol solvent with a ratio 1:1 was prepared. A silicon substrate and a small petri dish filled with DI water, which allowed the substrate to tilt

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at a 45° angle, were used in order to create the self-organized hexagonal closed-pack layer of PS nanoparticles at the interface. A pipette was used to gradually add the prepared PS solution to the petri dish until the PS solution was spread over the interface between DI water and air. Then using a pipette to add 10% SDS solution to the place where there were no PS nanoparticles to reduce the surface tension of water, then the PS nanoparticles shrunk and automatically packed up on the silicon surface. Completed samples were dried naturally, ready for the next step of the fabrication process of nanopillar structures [2, 3].

1.3. Reduction of PS nanospheres size

Oxygen plasma was used to etch PS nanoparticles isotropically in this step. For the etching process, the oxygen pressure was kept at 0.5 mbar, and the plasma power was at 480 W with varying duration 10 min, 15 min, 20 min, and 25 min. The higher the plasma duration was set, the smaller the size of PS nanoparticles remaining on substrates after plasma etching was obtained, thus having a direct consequence on the size of subsequent silicon nanopillars.

1.4. Deposition of silver layer

Here we use a thermal evaporator system to deposit a silver layer onto silicon substrates containing etched PS nanoparticles. The chamber was pumped down to 5×10^{-7} Torr to create a high vacuum condition, and then silver was evaporated by gradually increasing the current to around 70 A. The depositing rate needed to be small enough to form a uniform layer easily. The deposition of silver was kept until a thickness of about 100 nm was obtained, measured by a thickness sensor in the chamber. Lift-off of etched PS nanoparticles Substrates from the previous steps were put in a beaker containing cyclohexane. The beaker was then placed in an ultrasonic machine for one h at a temperature of 70°C. After this step, samples were dried naturally in a clean environment.

1.5. MACE

An HF 4.8 M solution was added with H₂O₂ 0.12 M or 1 M to prepare a suitable etchant, with a volume ratio of 1:1. A sample, after previous steps, was immersed in the solution with etching time varying from 30 min, 45 min, 60 min to 100 min. After MACE, the sample was rinsed in DI water and dried with a nitrogen gun [4].

2. Additional steps

After dispersing self-organized hexagonal closed-packed PS nanoparticles, the sample was annealed on a hot plate at 120°C for 5 min to immobilize all particles. Moreover, finally, the remaining silver layer was removed in HNO₃ solution (18 ml H₂O and 4 ml HNO₃ 68%) for 2 to 3 min, and then the sample was immersed in a MACE solution for 5 to 7 min to increase the hydrophobicity of the samples.

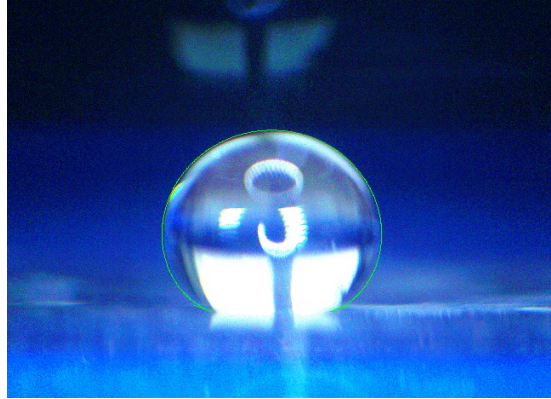


Figure 1: Typical photo of a water drop with contour fitting for deducing water contact angle.

3. Water contact angle measurement

For fitting the contour of a water drop, the Young-Laplace [5] is used as:

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P$$

Where R_1 and R_2 are the principal radii of curvature at any point on the drop. γ is surface tension, and ΔP is the pressure difference across the point at the surface. By expressing ΔP as the pressure at a certain height h plus the pressure of the apex curvature:

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta P_0 + \Delta \rho g h$$

$$\Delta P_0 = 2 \frac{\gamma}{b}$$

where b is the radius of curvature at the apex and $\Delta \rho$ is the difference between the weight density of water and the outside atmosphere. Finally

$$\frac{1}{R_1} + \frac{1}{R_2} = ch + \frac{2}{b}$$

$$c = \frac{\Delta \rho g}{\gamma}$$

When fitting the contour, for water $c = 134.753 \text{ (m}^{-2}\text{)}$. The fitting was performed by using a plugin of ImageJ software [6].

4. Total internal reflection effect

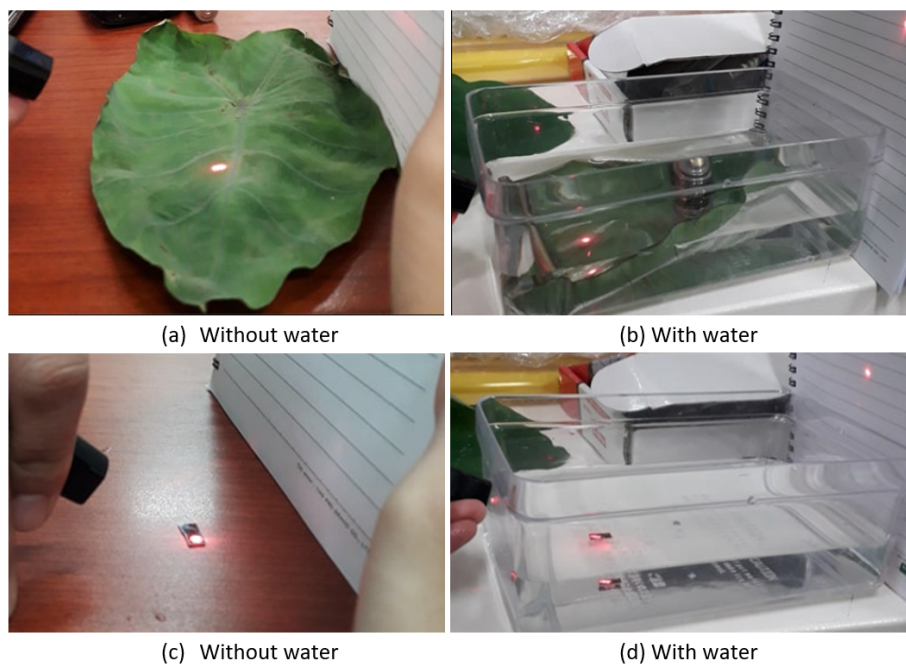


Figure 2: Demonstration of total reflection effect (a,b) on a taro leaf and (c,d) on etched silicon sample, without and with immersing in water. Reflected laser spots are observed only for SHS immersed in water.

5. Porous polymer

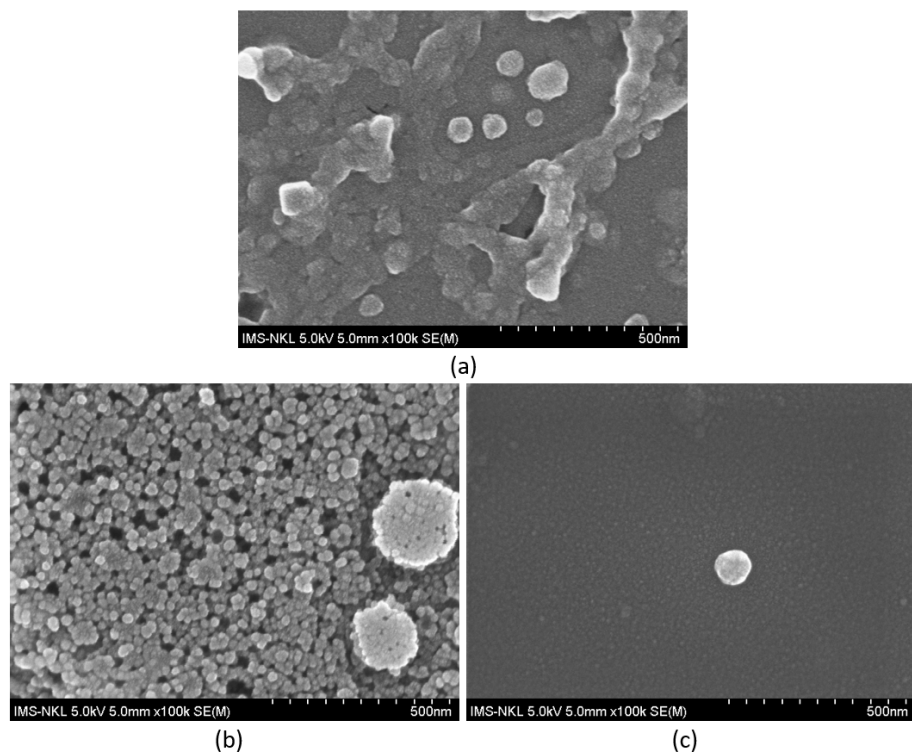


Figure 3: Typical porous PMMA surface after removing PS in THF: 5% of total polymer concentration (γ_p), (a) 20% [PMMA]/[PMMA]+[PS] (γ_{pm}), (b) 50% of γ_{pm} , and (c) 80% of γ_{pm} .

6. MACE

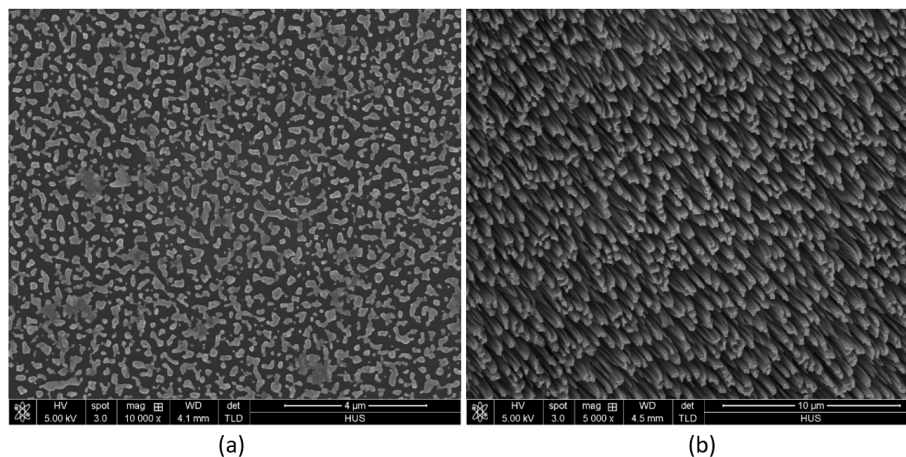


Figure 4: Typical morphology replication by MACE with 0.12M of H₂O₂ concentration: (a) the initial silver random patches were made just by annealing as deposited silver thin film, (b) a columnar structure made by MACE.

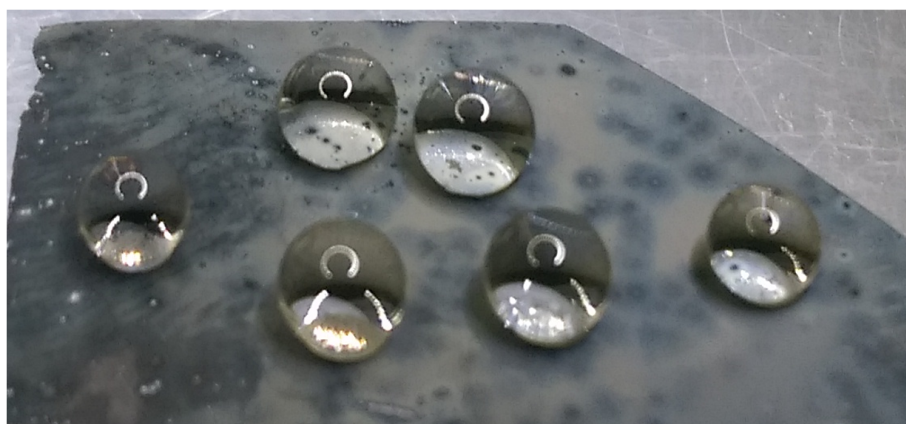


Figure 5: A selected photo of water drops on the etched silicon surface.

References

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