



Supporting Information

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Reversible Switching between Superhydrophilicity and Superhydrophobicity

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The Critical Contact Angle for Water Imbibition by Rough Surface

The critical CA (θ_c) for imbibition of water by a rough surface with roughness of r was calculated through equation (1)¹:

$$\cos \theta_c = \frac{1 - \phi_s}{r - \phi_s} \quad (1)$$

where ϕ_s is the solid fraction remained dry. When the wicking criterion is fulfilled, water can fill the grooves of the rough surface and only the upper part of the relief is not in contact with water. The surface roughness can be obtained by the AFM measurements. For the rough substrate with groove spacing of about 6 μm , the surface roughness is about 3.1, while the value of ϕ_s in the range of 0 ~ 0.25 (The value of 0.25 can be obtained through the width of microgrooves and groove spacing when assuming that the surfaces of the microconvexes are smooth, but they are rather rough because of the existence of nanostructures, therefore, ϕ_s is much less than 0.25, however, obviously larger than 0). So the value of critical contact angle can be calculated by equation (1) to be in the range of about 71 ~ 75°.

The effective contact angle (θ^*) of the rough surface is a function of ϕ_s and the contact angle of the flat surface (θ):

$$\cos \theta^* = 1 - \phi_s (1 - \cos \theta) \quad (2)$$

The superhydrophilicity of the rough substrate with groove spacing of about 6 μm below 29 $^\circ\text{C}$ can be explained by a very small value of ϕ_s due to the existence of nanostructures on the surfaces of microconvexes and microgrooves.

Potential Applications of the PNIPAAm Thin Film Modified Rough Surfaces

The PNIPAAm can be easily grafted onto other substrates to exhibit good thermal-responsive wettability if only they can provide or be modified to provide surface hydroxyls or other functional groups to react with bromoisobutyryl bromide and sufficient surface roughness. These materials are abundant, such as porous ceramics, cloth, and so on. This technique may have extensive applications in many fields.

1. Functional textile

Surfaces of most fabrics are very rough. Nature fabrics, such as cotton and woolen fabrics, often have surface hydroxyls or carboxyls, and for artificial fabrics, surface functional groups can be generated by different methods including plasma treatment and hydrolysis. Therefore, many fabrics can be transformed into functional textiles with thermal-responsive wettability by PNIPAAm modification. At high temperatures, the cloth is nonwetting with water, while at low temperatures, it can be wetted by water. These properties may have potential applications in both household and industrial fields.

2. Controllable drug release

PNIPAAm grafted hollow microball with porous shell (Fig. 1) can be utilized in controllable drug release. The drug can be filled into the cavities by immersing the microballs into the cold concentrated drug solution. At high temperatures, the hydrophobicity of the porous cavity wall can prevent drug solution in the cavity from diffusing outwards, while the it can be released by the capillary effect of the porous shell with hydrophilicity at low temperatures.

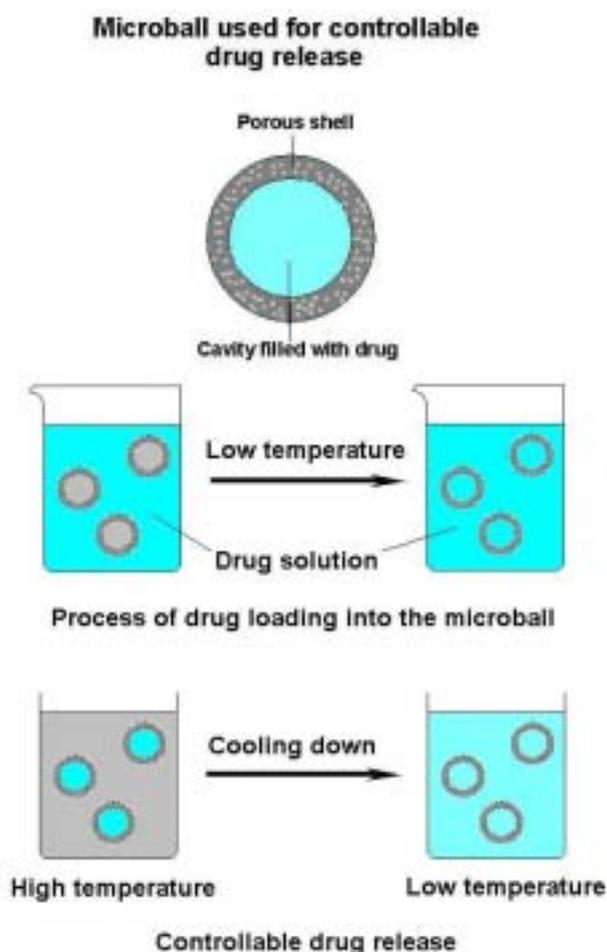


Fig. 1 Diagram of hollow microball with porous shell used in controllable drug release.

3. Temperature-controlled microfluidic switch.

By roughening a part of microfluidic channel and modifying its surface with PNIPAAm, it can serve as a temperature-controlled microfluidic switch that water or water solution can't pass at high temperatures, while can pass at low temperatures, as schematically shown in Fig. 2.

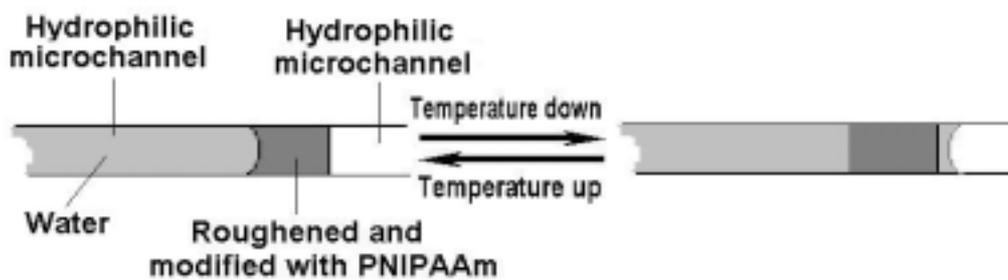


Fig. 2 Diagram for temperature-controlled microfluidic switch. The dark region is rough and modified with PNIPAAm. Water solution can pass at low temperatures because of capillary effect, while can't pass at high temperatures because the surface is very hydrophobic.

4. Thermal-responsive filter.

Roughened fiberglass mesh with PNIPAAm modification can also be used as a thermal-responsive filter that can be applied in oil/water separation and other applications.

For oil/water separation, at high temperatures, only oil can pass and the water was blocked, while at low temperatures, oil and water can all pass (Fig. 3).

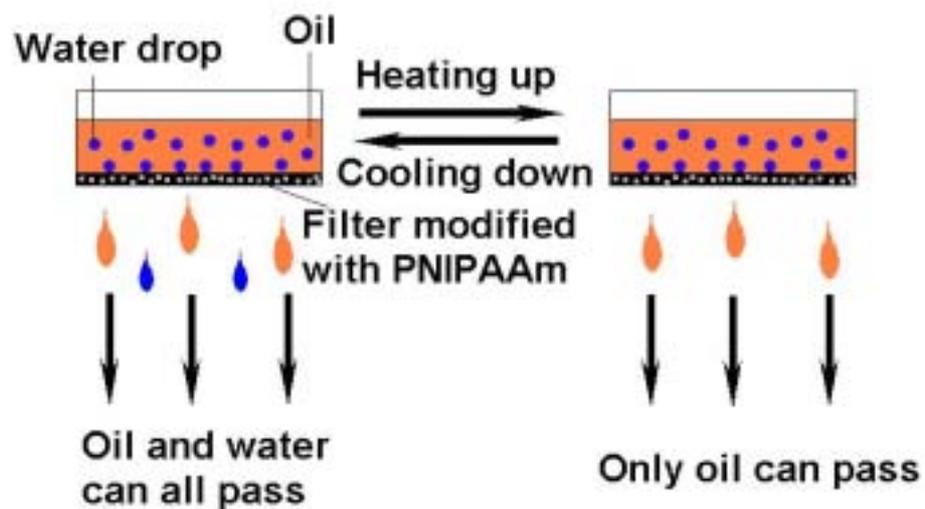


Fig. 3 Diagram of controllable oil/water separation with a thermal-responsive filter.

References:

1. Bico, J., Tord eux, C. & Quéré, D. Rough wetting. *Europhys. Lett.* **55**, 214-220 (2001)