

Surface Chemistry

A Super-Hydrophobic and Super-Oleophilic Coating Mesh Film for the Separation of Oil and Water**

Lin Feng,* Zhongyi Zhang, Zhenhong Mai,
Yongmei Ma, Biqian Liu, Lei Jiang,* and Daoben Zhu

Wettability is an important characteristic of solid surfaces and is controlled by the chemical composition and the geometrical

[*] Dr. L. Feng, Z. Zhang, Dr. Y. Ma, B. Liu, Prof. L. Jiang, Prof. D. Zhu
Organic Solid Laboratory, Center for Molecular Sciences
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (P.R. China)
Fax: (+86) 10-8262-7566
E-mail: fenglin@iccas.ac.cn
jianglei@iccas.ac.cn

Dr. L. Feng, Prof. Z. Mai
Laboratory for Soft Matter Physics
Institute of Physics, Chinese Academy of Sciences
Beijing 100080 (P.R. China)

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structure of the surface.^[1,2] Currently, the creation of a super-hydrophobic surface, with a water contact angle (CA) higher than 150°, has aroused great interest for both fundamental research and practical applications.^[3,4] It is reported that the hydrophobicity of a surface can be enhanced by surface roughness within a special size because air that is trapped between the droplet and the solid surface minimizes the contact area.^[5-8] Accordingly, various super-hydrophobic surfaces and films have been prepared by controlling the surface chemistry and surface roughness.^[9-23] However, no studies involving surfaces with both super-hydrophobic and super-oleophilic properties have been reported to date. It is considered that such surfaces can be used for the effective separation of oil and water.

In the study reported herein, we prepared a novel coating mesh film with both super-hydrophobic and super-oleophilic properties by a facile and inexpensive spray-and-dry method. The CA for water on this film is greater than 150°, and for diesel oil it is 0°. A homogeneous emulsion containing low-surface-energy material of polytetrafluoroethylene (PTFE) was used as the precursor. We believe that the nanostructured craterlike morphology on the microscale rough surface combined with the chemical composition contributes to these unique properties. The film can be used effectively for the separation of oil and water and is a feasible alternative to current separation methods.

Figure 1a shows the scanning electron microscopy (SEM) image of the large-area coating film. A stainless-steel mesh, whose pores have an average diameter of approximately 115 μm, was used as the substrate. No coating materials exist in the pores of the mesh, which ensures free passage of air through the prepared coating mesh film. Figure 1b is the enlarged image of the coating film; the rough structure of the surface is characterized by a ball- and blocklike morphology. The diameters of the balls are in a random distribution,

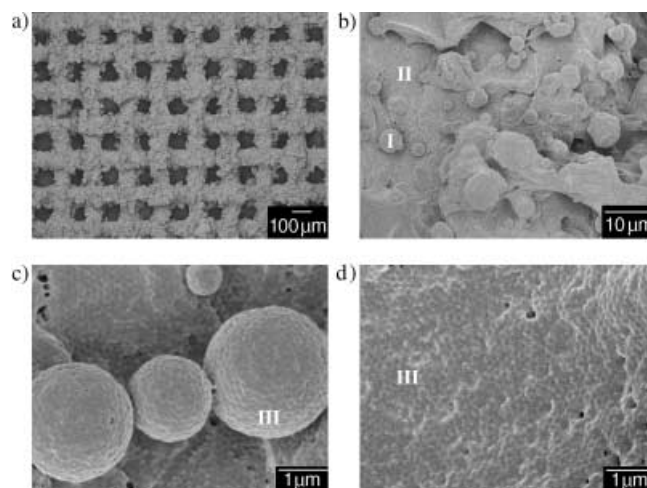


Figure 1. SEM images of the coating mesh film prepared from a stainless steel mesh with an average pore diameter of about 115 μm. a) Large-area view of the coating mesh film; b) enlarged view of the coating mesh film (the microstructured ball- (I) and blocklike (II) morphology is evident); c) and d) higher-magnification images of the balls and blocks observed in b), in which the nanostructured craters (III) can be clearly observed.

ranging from 2 to 5 μm , and some balls are glued to and embedded in each other. The blocks can be considered as an aggregation of balls. Figure 1c shows the high-resolution SEM image of the balls, whose structures resemble that of a golf ball: Craters with a diameter of about $71 \pm 8 \text{ nm}$ are densely and evenly distributed on the surface of each ball. The enlarged image of the blocks (Figure 1d) also shows the craterlike nanostructure similar to that of the balls. These results indicate that the prepared coating mesh film has a rough surface with both micro- and nanoscale structures, similar to that of the self-cleaning lotus leaf.^[24] The hydrophobicity and topology of the surface of the lotus leaf are a consequence of its special surface structure (branchlike nanostructures on top of micropapillae), which gives rise to a super-hydrophobic surface with a large CA and a small sliding angle. Therefore, the film is expected to show unusual wettability.

Figure 2a shows the shape of a water droplet on the prepared coating mesh film. The water CA in this case is about $156.2 \pm 2.8^\circ$, indicating that this film is super-hydro-

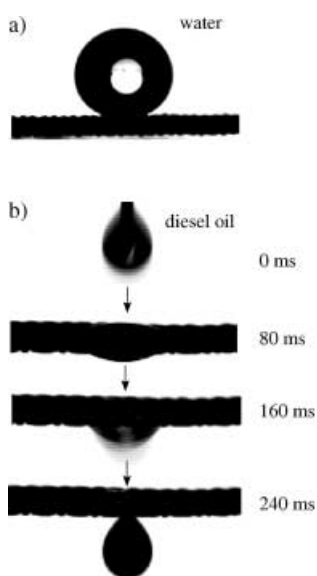


Figure 2. The prepared coating mesh film shows special wettability, with both super-hydrophobic and super-oleophilic characteristics. a) Shape of a water droplet on the coating mesh film with a contact angle of $156.2 \pm 2.8^\circ$ and sliding angle of 4° ; b) spreading and permeating behavior of a diesel oil droplet on the coating mesh film. The diesel oil spreads quickly on the coating mesh film and flows through (within only 240 ms).

phobic. The rough structures on the coating surface are believed to contribute to this property. In addition, the sliding angle of water on the film is about 4° (see Supporting Information). The water droplet is unstable on such films and spontaneously rolls off. The super-hydrophobic coating film is very hard and shows a needle hardness corresponding to the highest level (0 grade) of the Chinese Architectural Standard. This hardness is attributed to the chemical composition and the craterlike structures, which are reported to increase the hardness of super-hydrophobic surfaces.^[15b] More impor-

tantly, the hard super-hydrophobic coating mesh film has a practical application: The prepared film shows super-oleophilic properties, with a CA of about $0 \pm 1.3^\circ$. Figure 2b shows the spreading and permeating behavior of a diesel oil droplet on the coating mesh film. Oil spreads quickly on the film and permeates thoroughly within only 240 ms. This unique phenomenon of a film that exhibits both super-hydrophobic and super-oleophilic properties has, to our knowledge, not been reported before. This observation can be explained by Equation (1), first derived by Wenzel to describe the CA for a liquid droplet at a rough solid surface.^[7]

$$\cos\theta_r = r \cos\theta \quad (1)$$

In [Eq. (1)], θ is the intrinsic CA on a smooth surface, θ_r is that on a rough surface made of the same material, and r is the roughness factor. This equation indicates that with increasing surface roughness, the actual CA decreases for lyophilic materials ($\theta < 90^\circ$) and increases for lyophobic materials ($\theta > 90^\circ$). PTFE is a typical low-surface-energy material: The CA for water on a smooth PTFE film is about $121.6 \pm 1.8^\circ$, and for diesel oil it is $11.2 \pm 1.6^\circ$ (see Supporting Information), that is, PTFE is intrinsically hydrophobic and oleophilic. Clearly, the CA for water will increase and that for oil will decrease on the rough surface created by PTFE, according to Equation (1). Therefore, the PTFE-containing coating mesh film with both super-hydrophobic and super-oleophilic properties is induced. This film can be effectively applied to the separation of oil and water (see Supporting Information).

Various coating films can be designed by using the original meshes with different pore sizes as the substrates. Figure 3 shows the relationship between the pore diameter of the

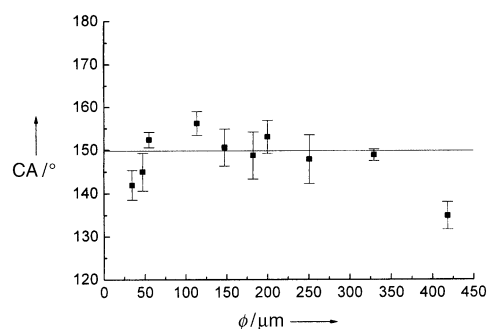


Figure 3. Relationship between the pore diameters of the original mesh and the water contact angles on the corresponding coating film. Clearly, the hydrophobicity of the coating mesh films is affected by the pore size.

original meshes and the CAs for water on the corresponding coating films. Within experimental and instrumental error, the CAs for water are about 150° on the coating mesh films with pore diameters of about 50–200 μm , but become smaller than 150° when the pore diameters are less than 50 μm or greater than 200 μm . In comparison, the CAs for diesel oil on these films are all smaller than 4° . These results indicate that the hydrophobicity of the coating mesh films is affected by the size of the pores. According to Figure 3, the *optimum* pore

diameter of the film is 50–200 μm , beyond which superhydrophobicity cannot be realized. Hence the pore diameter of the original mesh substrate is very important to the wettability of the final coating film. Accordingly, high-quality coating films can be prepared by judicious selection of the original meshes and careful design of the composition and structure. The prepared films can be used continuously, and the coating materials do not shed off. Furthermore, since the coating films have all the properties of the original mesh such as hardness, porosity, and better resistance to corrosive liquids such as acids and alkalis, they are suitable for practical and industrial applications.

In summary, a novel interfacial material of hard coating mesh film with both super-hydrophobic and super-oleophilic properties was prepared by the fabrication of micro- and nanostructured rough surfaces from a fluorine-containing material. The separation of diesel oil and water in this study was very efficient, which is suitable for many practical applications. The coating composition and the preparation technology can be expanded to the manufacture process to provide functional separation and filtration equipment.

Experimental Section

A homogeneous emulsion containing teflon (polytetrafluoroethylene, PTFE, 30 wt%), adhesive (polyvinyl acetate, PVAc, 10 wt%), dispersant (polyvinyl alcohol, PVA, 8 wt%), surfactant (sodium dodecyl benzene sulfonate, SDBS, 2 wt%), and thinner (distilled water, 50 wt%) was prepared by mixing them in proportion and agitating thoroughly. The stainless steel mesh substrates (pore diameters: 30–420 μm) were scrubbed to remove rust, washed, and dried. The emulsion was then sprayed evenly on the selected mesh screen with dry compressed air (0.6 MPa). Subsequently, the coated mesh was placed in an oven for about 30 min at 350 $^{\circ}\text{C}$ (to decompose the adhesive, dispersant, and surfactant into gases such as H_2O and CO_2 and to evaporate the thinner), resulting in a coating mesh film with a rough surface composed mainly of low-surface-energy PTFE.

The SEM images were obtained on a JEOL JSM-6700F scanning electron microscope at 3.0 kV. The contact angles were measured on a Dataphysics OCA20 contact-angle system at ambient temperature. Water or diesel oil droplets (about 5.0 μL) were dropped carefully onto the coating films. The contact angle value was obtained by measuring five different positions of the same sample. The film hardness was evaluated by a needle test according to the Chinese Architectural Standard (GB/T9286-1998) test.

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