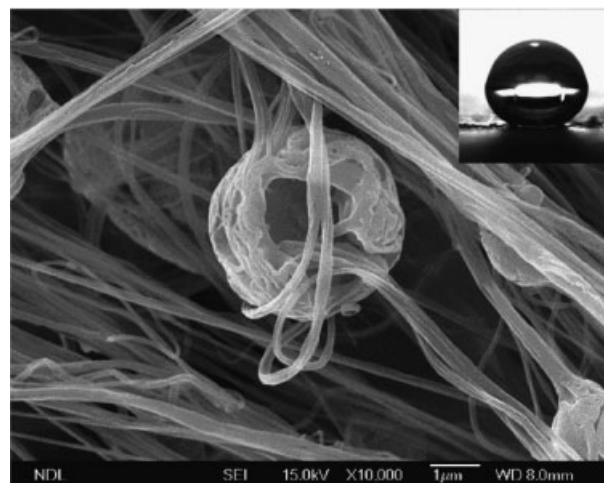


Fabrication of Superhydrophobic and Superoleophilic Polystyrene Surfaces by a Facile One-Step Method

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A facile one-step method has been developed to prepare both superhydrophobic and superoleophilic surfaces of polystyrene (PS) without any chemical modification. A rough film consisting of micro-bead and nano-fiber mixed structures is formed by spraying a PS solution onto a large area and any type of substrate. The mixed structures with such unique wettability properties can be used in oil/water separation and as oil sorbents.



Introduction

The wettability of a solid surface is an important property of materials in industrial, environmental, and biological applications.^[1] During the past few decades, superhydrophobic surfaces with water contact angles (CAs) larger than 150° have found numerous potential practical

applications, such as self-cleaning surfaces, prevention of the adhesion of snow, and others.^[2] In general, both surface chemistry and roughness can affect the wettability of water and oil. The water CA on a smooth surface of a hydrophobic material is typically in the order of 100 to 120°,^[3] but can reach values higher than 150° with roughness or hierarchical micro/nano-structures.^[4,5] For example, the water CA of the natural lotus leaf can be higher than 160° because of its waxy coating with rough surface, and it is able to trap air between the water droplets and the wax crystals at the plant surface to minimize the contact area.^[6,7] Inspired by self-cleaning lotus leaves, superhydrophobic surfaces have been prepared by using various methods such as fractal surface,^[4] plasma treating polymer surfaces,^[8–10] functionalizing roughened substrates with perfluoroalkyl groups,^[11] densely packing aligned carbon nanotubes,^[6,12,13] self-assembled monolayers of *n*-alkanoic acids on electroche-

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mically deposited copper films,^[14] and other approaches.^[15] However, the drawbacks of these fabrications include that they are too complicated, expensive, time-consuming, and restricted to only certain types of substrates.

In order to overcome these disadvantages, a great deal of effort has been put towards simplifying the process by employing low-cost commercially available polymers. Erbil et al. described a superhydrophobic film with a rough surface of poly(propylene) formed by proper selection of solvents and temperatures.^[16] Jiang et al. reported the preparation of microsphere/nanofiber superhydrophobic polystyrene films by a simple electrospinning method.^[17] They also reported that both superhydrophobic and a superoleophilic film can be fabricated by using the block-like structure of a poly(tetrafluoroethylene) film.^[18]

In addition to the superhydrophobic surface, the oil/water separation process and water preservation are also important for various applications in industry as well as daily life. Among the main existing technologies, the use of a sorbent is important to induce separation of oil and water such that the oil can be easily recovered.^[19] The sorbent for such a purpose should possess a high oleophilic and hydrophobic property.

Herein, we report a novel simple one-step procedure to produce superhydrophobic and superoleophilic polystyrene (PS) films by an airbrush method. PS is a commercial polymer with slight hydrophobicity and oleophilicity and possesses a water and oil CA of $93 \pm 2.5^\circ$ and $6 \pm 2.7^\circ$, respectively. An airbrush is a common tool for artists when creating spray paints. The fact that sprayed liquid jets of macroscopic dimensions break up into fine droplets has been of great scientific interest and application.^[20] In this study, the water CA on this airbrush produced film is found to be larger than 150° , and the diesel oil CA is 0° , respectively. These superhydrophobic PS films are cheap, facile, and fast to process, suitable for any type and shape of substrate. Furthermore, they can also be used for oil/water separation as well as for an oil sorbent.

Experimental Part

PS with an $\overline{M}_n = 181\,000$ and PDI = 1.78 was purchased from Chi-Mei Corp, Taiwan, which was reprecipitated from methanol by dissolving in tetrahydrofuran (THF), and then dried in a

vacuum oven at 60°C for 12 h. To prepare the superhydrophobic films, PS was first dissolved in THF solvent at various concentrations of 2, 4, and 10 wt.-%. The polymer solution was fed into a receptacle of an airbrush, and then sprayed evenly on a sheet glass (area of $100 \times 100 \text{ mm}^2$) with dry compressed air (100 kPa). The flow rate of the polymer solution spraying on the subject was controlled at $0.2 \text{ mL} \cdot \text{s}^{-1}$ and the distance between the nozzle and substrate was set at 150 mm. The total amount of PS sprayed on the substrate was ca. 0.1 g and the spraying time was dependent on the polymer solution concentration. The operating parameters are summarized in Table 1. The test of the sorption of oil is based on a literature procedure.^[21] Into a beaker that contained 500 mL of water at room temperature, the pollutant (diesel oil, 140 mL) was poured to obtain a layer of about 1 cm above the water. The PS film (1 g) made from a 10 wt.-% solution was placed on the pollutant. The PS film was left to drip for 20 min and weighed after sorption. The morphologies of the polymer surfaces were characterized by scanning electron microscopy (SEM) (JOEL JSM 6500F Tokyo, Japan). Contact and sliding angles were measured on a Krüss GH-100 contact angle goniometer at ambient temperature by injecting a $5 \mu\text{L}$ water droplet. All reported contact angles are the average of six measurements.

Results and Discussion

Figure 1a displays the SEM image of the airbrushed PS film morphology prepared from a 2 wt.-% solution of PS in THF, which shows a rough surface with many polymer droplets. This film possesses randomly distributed irregular micro-beads (diameters ranging from 0.5 to $7.0 \mu\text{m}$) and some nano-fibers around the polymer beads (average diameter = 75 nm). The irregular hollow structures of these beads and nano-fibers on the surface can be clearly observed from an enlarged view shown in Figure 1b. These micro-beads and nano-fibers are formed by two stages during the spraying process. During the first stage, the surface tension tends to break the solutions of the polymer jets into fine droplets as a result of Rayleigh instability.^[22–24] The fast evaporation rate of the THF in the solution droplets leads to a time-dependent non-uniform concentration and a temperature gradient on the way to the substrate surface.^[25] During the second stage, the outer shell of these polymer droplets solidifies and the residual solvent evaporates out of the droplets, which causes the droplets to wrinkle, crumple, and shrink to form irregular particles where the solvent rich regions are transformed

Table 1. Solution concentrations, operating parameters, water contact angles, and the morphologies of the airbrushed PS film.

Concentration	Flow rate	Spraying time	Contact angle	Main morphology	Sub-structure
wt.-%	$\text{mL} \cdot \text{s}^{-1}$	s			
2.0	0.2	25.0	$113 \pm 1.3^\circ$	Rough films	Beads and fibers
4.0	0.2	10.0	$155 \pm 1.6^\circ$	Beads and fibers	Rough films
10.0	0.2	5.0	$\approx 140^\circ$	Fibers	Beads

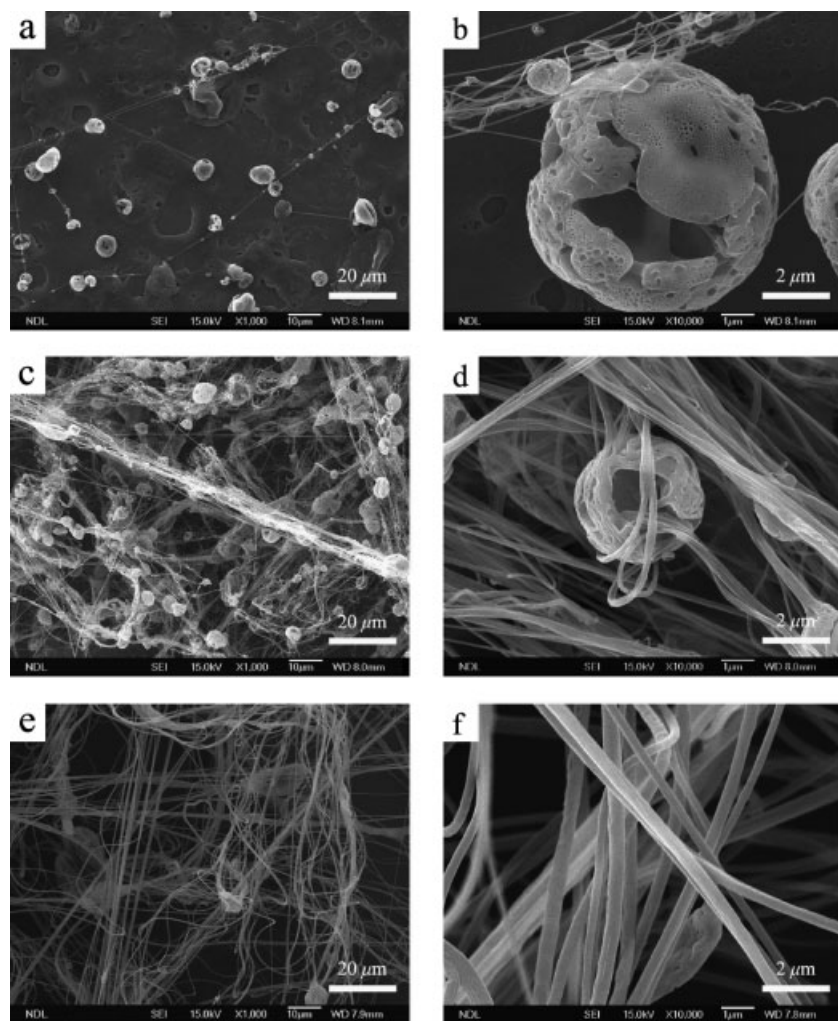


Figure 1. SEM micrographs of the airbrushed PS film prepared from the solution concentrations of a) 2, c) 4, and e) 10 wt.-% PS; b), d), and f) are the magnification corresponding to a), c), and e), respectively.

into pores. In addition, the portion of the polymer solution with locally high concentration possesses sufficient chain entanglements and high viscosity. This reduces the breakup rate of the solution jets, which is lower than the solvent evaporation rate, and results in nano-fibers on the pathway.^[20,26] The water CA ($\approx 113^\circ$, Figure 2b) on the resultant mixed structures that consist of few micro-beads and nano-fibers is slightly higher than that of the spin-coated smooth PS film ($\approx 93^\circ$, Figure 2a). However, this CA value remains too low to be classified as a superhydrophobic surface.

The solution viscosity increases from 2.36 to 6.44 centipoises as the solution concentration increases from 2 to 4 wt.-%. The higher solution viscosity further promotes the number of the chain entanglements and changes the flow behavior. The resultant morphology shows that more beads and fibers coexist, as shown in Figure 1c and 1d. This morphology is similar to, but more irregular than, the

reported morphology obtained by the electrospinning method.^[17,27–31] This mixed structure gives a water CA of $\approx 155 \pm 1.6^\circ$ (Figure 2c) and a sliding angle of $\approx 6^\circ$, which indicates that the film is rough enough to trap air between the water droplets and the PS surface.

As the solution concentration further increases to 10 wt.-%, the viscosity of the solution quickly increases to 48.80 centipoises. The resultant morphology shows network structures that contain longer and thicker fibers with diameters ranging from 170 to 410 nm. Polymer particles have nearly disappeared, as shown in Figure 1e and 1f, which indicates that the solution viscosity and chain entanglement are both high enough to create a long thread without breaking up into droplets before solidifying on the surface. The photo image of the water CA on such a film with nano-fibers is shown in Figure 2d. Since the water droplet is partially sunk into the film surface, the boundary between the water and substrate is unclear, and thus the water CA can not be measured accurately. However, the water CA can still be estimated at $\approx 140^\circ$. A water droplet is still unstable on this film and spontaneously rolls off with a sliding angle of 10° .

According to Cassie's law for surface wettability,^[32] hydrophobicity is related to the contact area between the water and the material. The contact angle θ_c for a heterogeneous surface can be expressed as follows:

$$\cos \theta_c = f_1 \cdot \cos \theta_1 - f_2 \cdot \cos \theta_2 \quad (1)$$

where f_1 and f_2 are the surface area fractions of components 1 and 2, respectively. θ_1 and θ_2 are the contact angles of the flat film of components 1 and 2, respectively. When component 2 is air with a water CA of 180° , Equation (1) can be expressed as Equation (2):

$$\cos \theta_c = f_1 \cdot \cos \theta_1 - f_2 = f_1 \cdot (\cos \theta_1 - 1) - 1 \quad (2)$$

This equation predicts that increasing the fraction of the air (f_2) can also increase the contact angle of the film. Given the CA of a smooth PS surface, the f_1 of

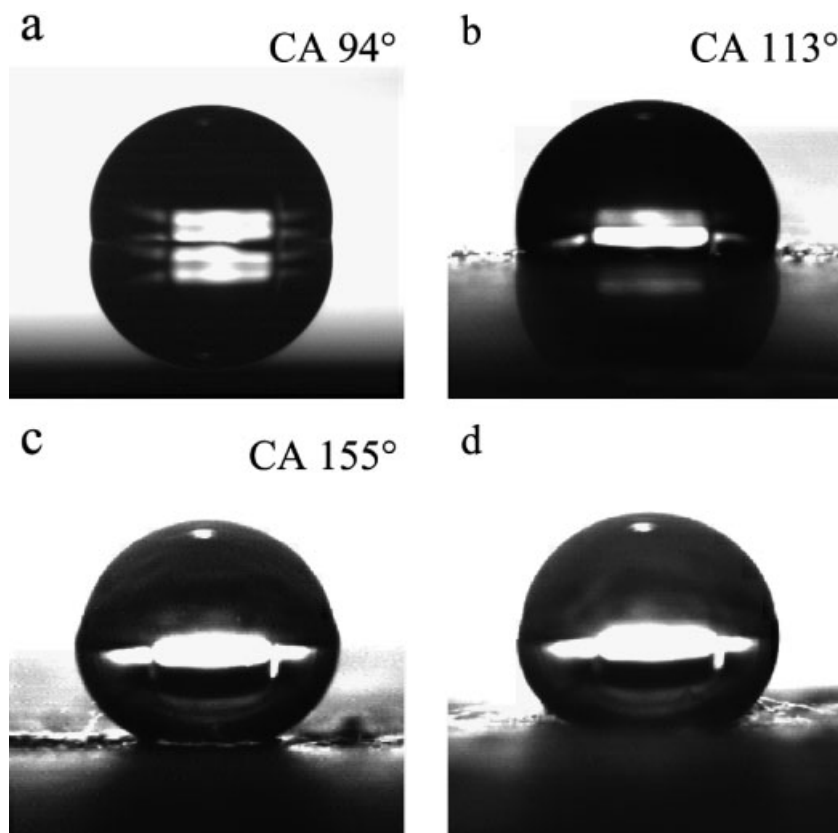


Figure 2. a) Profile of water drops on a smooth PS film, b), c), and d) are the images of water droplets on the airbrushed PS film prepared from the solution concentrations of 2, 4, and 10 wt.-%, respectively.

the airbrushed film made from a 4 wt.-% (CA = 155°) concentration solution is calculated to be 0.057, which indicates that the contact area fraction of the water and the airbrushed PS film is very low. Therefore, the water is mainly sustained by an air cushion. The airbrushed film that contains micro- and nano-scale mixed structures can be regarded as a heterogeneous surface.

Compared with the water CA on these airbrushed films, the observation of the oil CA can be explained by Equation (3) derived from Wenzel, which describes a liquid droplet on a rough solid surface.^[33]

$$\cos \theta_w = r \cdot \cos \theta_0 \quad (3)$$

where θ_w is the equilibrium CA on a rough surface, θ_0 is the intrinsic CA on a smooth surface, and r is the roughness factor. The ratio of the true surface area A (taking into account the peaks and the valleys on the surface) to the apparent surface area A' is defined as the roughness factor = A/A' . This equation indicates that in the Wenzel oleophilic state, the surface oleophilicity can be enhanced by increasing the surface roughness, and the oil droplet can penetrate into the surface cavities. Since polystyrene is an oleophilic material and if the surface is in the form of a mixed micro-bead and nano-fiber structure, these films

show superoleophilicity if the concentration of the prepared solutions are higher than 4 wt.-%. The diesel oil can be totally wetted through the capillary force between the gaps among these PS particles or fibers. Therefore, these PS fibers can function as an oil sorbent. In our experiment, the sorption capacity of these PS fibers (weight of pollutant taken up by one gram of sorbent) can reach up to 21.6 g per g of sorbent.

In addition, the PS fiber coating on a stainless steel mesh can serve as oil/water separator. A 10 wt.-% PS solution was sprayed evenly on a steel mesh (pore diameters: 300 μm). At this concentration, the solution viscosity is high enough to generate network structures of dense PS fibers on the steel mesh without forming thin films and blocking up the pores of the mesh. The mesh, moreover, can be made from many kinds of materials with differing pore diameters, and acts as a scaffold to prop the PS fibers and reinforce the structures. With such a special wettability of the network fibers spread on the steel mesh, oil droplets can fully wet the rough PS surface by capillary forces and then penetrate the steel mesh by gravity force. When the oil enters the gaps of these fibers, component 2 in Equation (1) is replaced by the oil, and the water CA is reduced to about 110° on the surface of the oil-wetted PS fibers, as shown in Figure 3a. However, the water is still

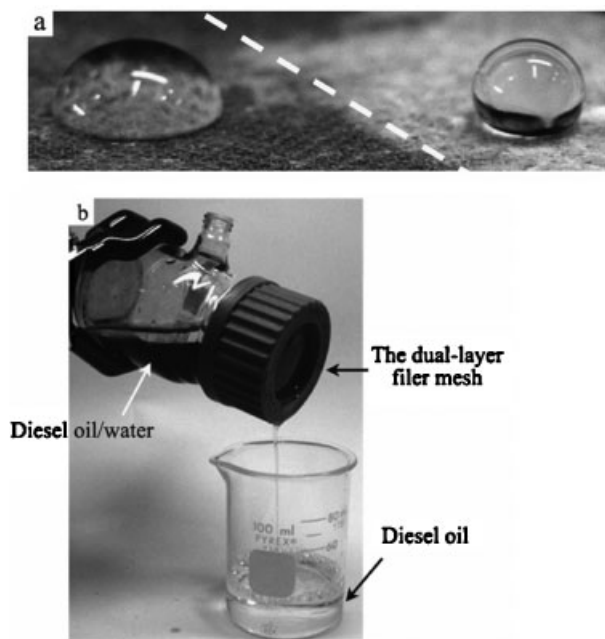


Figure 3. a) Optical image of a 100 μL water droplet on the dual-layer filter mesh. It has a lower water CA on the oil-wetted PS surface (left) than on the unwetted PS surface (right). b) The separation of diesel oil and water was efficient with the dual-layer filter mesh (water was stained with black ink).

isolated by the network structures of the PS fibers. Therefore, this dual-layer filter mesh can be applied to separate oil and water (Figure 3b) and the separation efficiency of water and diesel oil is calculated to be up to 95 wt.-%.

Conclusion

We have demonstrated a convenient method to fabricate a superhydrophobic and superoleophilic PS film that consists of a mixture of micro-bead and nano-fiber structures. The morphology of this airbrushed film is more irregular, but the cost is less and fabrication is faster than that prepared by the electrospinning method. The network structures of the PS fibers can act as an oil sorbent and can separate water and diesel oil. It is believed that the simple airbrush method described here is suitable to prepare large area and different shapes of superhydrophobic surfaces from various materials, and wide industrial applications are anticipated.

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- [1] P. Aussillous, D. Quere, *Nature* **2001**, *411*, 924.
- [2] P. Ball, *Nature* **1999**, *400*, 507.
- [3] A. Hozumi, O. Takai, *Thin Solid Films* **1997**, *303*, 222.
- [4] T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125.
- [5] T. L. Sun, L. Feng, X. F. Gao, L. Jiang, *Acc. Chem. Res.* **2005**, *38*, 644.
- [6] L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, J. Zhai, Y. L. Song, B. Q. Liu, L. Jiang, D. B. Zhu, *Adv. Mater.* **2002**, *14*, 1857.
- [7] S. Herminghaus, *Europhys. Lett.* **2000**, *52*, 165.
- [8] M. Morra, E. Occhiello, F. Garbassi, *Langmuir* **1989**, *5*, 872.
- [9] I. Woodward, W. C. E. Schofield, V. Roucoules, J. P. S. Badya, *Langmuir* **2003**, *19*, 3432.
- [10] C. F. Wang, S. F. Chiou, F. H. Ko, C. T. Chou, H. C. Lin, C. F. Huang, F. C. Chang, *Macromol. Rapid Commun.* **2006**, *27*, 333.
- [11] K. Tsujii, T. Yamamoto, T. Onda, S. Shibuichi, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1011.
- [12] K. K. S. Lau, J. Bico, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, G. H. McKinley, K. K. Gleason, *Nano Lett.* **2003**, *3*, 1701.
- [13] H. J. Li, X. B. Wang, Y. L. Song, Y. Q. Liu, Q. S. Li, L. Jiang, D. B. Zhu, *Angew. Chem. Int. Ed.* **2001**, *40*, 1743.
- [14] S. T. Wang, L. Feng, H. Liu, T. L. Sun, X. Zhang, L. Jiang, D. B. Zhu, *ChemPhysChem* **2005**, *6*, 1475.
- [15] H. Yabu, M. Shimomura, *Chem. Mater.* **2005**, *17*, 5231.
- [16] H. Y. Erbil, A. L. Demirel, Y. Avci, O. Mert, *Science* **2003**, *299*, 1377.
- [17] L. Jiang, Y. Zhao, J. Zhai, *Angew. Chem. Int. Ed.* **2004**, *43*, 4338.
- [18] L. Feng, Z. Y. Zhang, Z. H. Mai, Y. M. Ma, B. Q. Liu, L. Jiang, D. B. Zhu, *Angew. Chem. Int. Ed.* **2004**, *43*, 2012.
- [19] G. Deschamps, H. Caruel, M. E. Borredon, C. Bonnin, C. Vignoles, *Environ. Sci. Technol.* **2003**, *37*, 1013.
- [20] M. Moseler, U. Landman, *Science* **2000**, *289*, 1165.
- [21] J. Croquette, C. Bocard, *Oil Petrochem. Pollut.* **1983**, *1*, 261.
- [22] L. Rayleigh, *Proc. London Math. Soc.* **1878**, *10*, 4.
- [23] T. R. Powers, D. F. Zhang, R. E. Goldstein, H. A. Stone, *Phys. Fluids* **1998**, *10*, 1052.
- [24] T. R. Powers, R. E. Goldstein, *Phys. Rev. Lett.* **1997**, *78*, 2555.
- [25] S. C. Luo, V. Craciun, E. P. Douglas, *Langmuir* **2005**, *21*, 2881.
- [26] C. Wagner, Y. Amarouchene, D. Bonn, J. Eggers, *Phys. Rev. Lett.* **2005**, 95.
- [27] Z. Z. Gu, H. M. Wei, R. Q. Zhang, G. Z. Han, C. Pan, H. Zhang, X. J. Tian, Z. M. Chen, *Appl. Phys. Lett.* **2005**, 86.
- [28] M. Ma, R. M. Hill, J. L. Lowery, S. V. Fridrikh, G. C. Rutledge, *Langmuir* **2005**, *21*, 5549.
- [29] M. Ma, Y. Mao, M. Gupta, K. K. Gleason, G. C. Rutledge, *Macromolecules* **2005**, *38*, 9742.
- [30] H. Fong, I. Chun, D. H. Reneker, *Polymer* **1999**, *40*, 4585.
- [31] K. H. Lee, H. Y. Kim, H. J. Bang, Y. H. Jung, S. G. Lee, *Polymer* **2003**, *44*, 4029.
- [32] A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546.
- [33] R. N. Wenzel, *Ind. Eng. Chem. Res.* **1949**, *28*, 988.