

Superhydrophobic Surface**A Lotus-Leaf-like Superhydrophobic Surface: A Porous Microsphere/Nanofiber Composite Film Prepared by Electrohydrodynamics****

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Inspired by self-cleaning lotus leaves, superhydrophobic surfaces with water contact angles (CA) larger than 150° have attracted great interest over the last few years for both fundamental research and practical applications. The fundamental mechanism of this phenomenon proposes that a combination of a hierarchical micro/nanostructure and low-

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[**] The authors thank the State Key Project for Fundamental Research (G1999064504) and the Special Research Foundation of the National Nature Science Foundation of China (29992530) for continuing financial support. The Chinese Academy of Sciences is gratefully acknowledged.

surface-energy materials are essential for superhydrophobicity.^[1] To fabricate such surfaces, various methods have been proposed, such as the solution method,^[2] the sol-gel method,^[3] solidification of alkylketene dimer,^[4] the plasma fluorination method,^[5] and others.^[6–9] We have already made some progress in this field. For example, we prepared superamphiphobic films of aligned carbon nanotubes with fluoroalkylsilane coating.^[10] Furthermore, aligned polymer nanofiber films with superhydrophobic properties were fabricated by a template method.^[11] Recently, several thermally or optically responsive smart interfacial materials that can switch between superhydrophilicity and superhydrophobicity were reported.^[12]

The electrohydrodynamics (EHD) technique has proved to be a versatile and effective method for manufacturing micro- to nanoscale fibers or particles from a variety of materials, such as polymers,^[13] inorganic,^[14] and hybrid (organic/inorganic)^[15] compounds, for a broad range of applications in membrane technology,^[16] tissue engineering,^[17] optical^[18] and biosensors,^[19] and drug delivery.^[20] Here we report the preparation of a lotus-leaf-like porous microsphere/nanofiber composite film of polystyrene (PS), a cheap industrial polymer, by a simple EHD method, which for the first time afforded superhydrophobicity ($CA = 160.4^\circ$) without any modification.

In a typical EHD process, a sample solution is pumped through a nozzle to which a high voltage is applied relative to a grounded metal plate (collector) to form an electrically charged jet of solution. The solution jet solidifies with accompanying evaporation of solvent and forms a film on the collector.^[21] We prepared EHD films with different morphologies from PS/DMF solutions of different concentrations at a constant distance between the tip and collector of 14 cm and an applied voltage of 14 kV.

Nanofibrous film I was first fabricated from a 25 wt% solution of PS in DMF. Figure 1 a and b show SEM images of film I. The nanofibers are randomly oriented on the substrate, and the individual fibers have high slenderness ratios. The

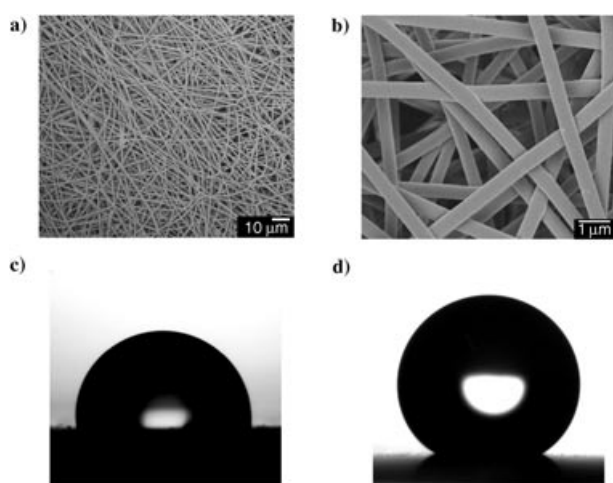


Figure 1. a) SEM image of film I prepared from a 25 wt% PS/DMF solution; b) magnified part of (a); water droplets on a spin-coated PS film (c) and on film I (d).

average diameter of the fibers is 420 nm, and they are longer than several millimeters. Film I has a network structure because numerous fibers interweave integrally like a spider's web. The wetting properties of film I were investigated. Compared with a native PS surface prepared by spin coating (water $CA = 95.1 \pm 0.3^\circ$, Figure 1 c), film I has a much higher water CA of $139.1 \pm 1.8^\circ$ (Figure 1 d), that is, the hydrophobicity of film I is improved to some extent because of the network structure.

Next a dilute PS/DMF solution (5 wt%) was used to fabricate microparticle film II. The particles, diameters of which range from 2 to 7 μm , exhibit a hollow conical shape (Figure 2 a), as a result of constriction and collapse during

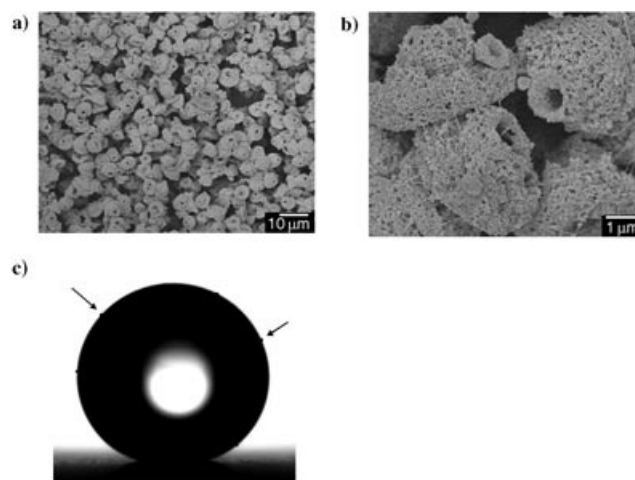


Figure 2. a) SEM image of film II fabricated from a 5 wt% PS/DMF solution; b) magnified image of porous microparticles; c) water droplet on film II (the dots on the droplet, indicated by arrows, are clusters of particles separated from the film).

solidification of the solution droplets upon evaporation of solvent in the EHD process. A more highly magnified image shows that the microparticles are covered by nanopillars of 50–70 nm (Figure 2 b). Thus the surface roughness of film II is greater than that of film I. Since surface roughness is a very important factor in wetting,^[1] it can be deduced that film II should be more hydrophobic than film I. Wettability measurements confirmed this hypothesis and showed that film II is superhydrophobic with a water CA of $162.1 \pm 1.0^\circ$ (Figure 2 c). However, during CA measurements, some clusters of microparticles separated from the substrate spontaneously and floated on water droplets (arrows in Figure 2 c) because the density of porous PS microparticles is lower than that of water. This drawback prevents its further application.

Accordingly, a stable superhydrophobic EHD film should be realizable by building a composite structure of films I and II that has both the structural stability of nanofibers and the superhydrophobicity of porous microparticles. There have been a few reports on the formation of bead-fibers when uniform fibers are fabricated,^[22–25] but most of them concentrate on preparing fibers while neglecting to investigate the properties of the bead-fibrous film. Here we pay more attention to investigating the porous microsphere/nanofiber

composite film (PMNCF) with its unique structure, which was prepared from a 7 wt % PS/DMF solution. The SEM image of the as-prepared film (Figure 3a) shows numerous microspheres and nanofibers distributed densely over the whole

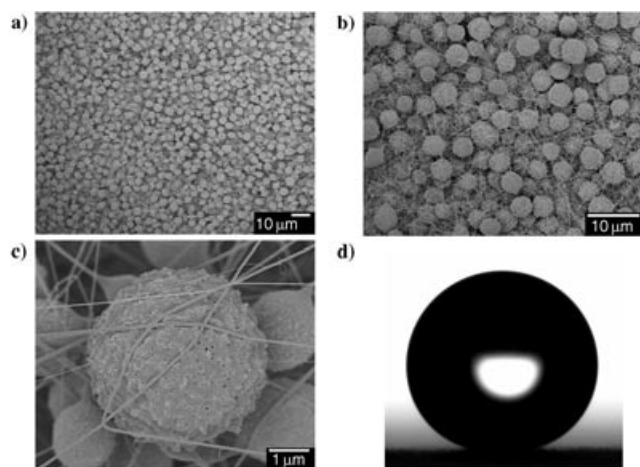


Figure 3. a) SEM image of PMNCF prepared from a 7 wt % PS/DMF solution; b) 3D network structure of PMNCF; c) surface nanostructure of a single porous microsphere; d) water droplet on PMNCF.

substrate. Almost every microsphere is interlinked with nanofibers, and the nanofibers are interwoven in a stable multilayer 3D network in which the microspheres are embedded (Figure 3b). A more highly magnified image indicates the presence of many protuberances and cavities with dimensions of tens to hundreds of nanometers on the surfaces of the microspheres (Figure 3c). The sizes of the microspheres and nanofibers are 3–7 μm and 60–140 nm, respectively. The water CA of the PMNCF is $160.4 \pm 1.2^\circ$ (Figure 3d), that is, it shows stable superhydrophobicity. In other words, PMNCF combines the advantages of films I and II while overcoming the disadvantages of both. Moreover, the morphologies of the EHD products could be easily controlled by merely adjusting the concentration of the solution.

The morphologies of the EHD products method are mainly influenced by the concentration of the solution, the solvent, the electric potential, and the nozzle-to-collector distance.^[22] Of these, the solution concentration and solvent are crucial for the film morphology, while the electric potential and distance have less influence for a given solution. As a consequence of the effect of surface tension, the liquid jet prefers to shrink to spherical droplets to acquire the smallest surface area. In the EHD process, however, the solution jet is placed in a strong electric field, so competition between electrical force and surface tension decides the morphology of the product. When a concentrated solution (20–30 wt %) is used, the high viscosity and polymer content make the solution jet elongate and solidify quickly, and ultrafine fibers are formed. With dilute solutions (3–5 wt %), the very low viscosity does not suffice to sustain the elongation of the liquid jet, and therefore the thin jet of solution leaving the nozzle instantly shrinks to droplets and ultimately forms microparticles. The formation of PMNCF is

a mesostate of these two conditions (6–10 wt %), in which one part of the liquid jet shrinks to spheres, and the other solidifies to fibers.

In PMNCF, the porous microspheres of PMNCF play the leading role in the superhydrophobicity, while nanofibers act as a skeleton that reinforces the composite film. It has long been known that lotus leaves show excellent water-repellent properties, and much attention has been paid to constructing biomimetic self-cleaning materials on the basis of the lotus-leaf effect. The superhydrophobicity of the lotus leaf is due to surface roughness caused by branchlike nanostructures on top of the micropapillae and the low surface energy epicuticular wax.^[1b] Similarly, the surfaces of as-prepared PMNCF are composed of micro- and nanoscale structures. Additionally, PS is a low surface energy material because of its CH groups. The micro/nano hierarchical structures increase surface roughness dramatically, so that air can be trapped in the aperture of porous microspheres and nanofibers. It is known that the air trapped in the surface is very important to hydrophobicity, because the water CA of air is regarded to be 180° . Cassie and Baxter proposed Equation (1) to describe the relationship between the CA of a water droplet on a smooth surface (θ) and the CA on a heterogeneous surface (θ_{CB}) composed of a solid and air.^[26]

$$\cos \theta_{\text{CB}} = f_1 \cos \theta - f_2 \quad (1)$$

Here, f_1 and f_2 are the fractions of solid surface and air in contact with liquid, respectively, that is, $f_1 + f_2 = 1$. Given the water CAs of a native PS surface and PMNCF, f_2 is calculated to be 0.934, which indicates that the achievement of superhydrophobicity by PMNCF is mainly a result of the air trapped in the rough surface by combining microstructures of spheres with nanostructures of protuberances and cavities.

In conclusion, a superhydrophobic PS film with a novel composite structure consisting of porous microspheres and nanofibers has been prepared by the versatile EHD method. The morphologies of EHD products could be controlled by adjusting the concentration of the starting solution. The porous microspheres contribute to the superhydrophobicity by increasing surface roughness, while nanofibers interweave to form a 3D network that reinforces the composite film. We believe that the EHD method described here could easily be extended to preparing stable superhydrophobic surfaces from a wide variety of materials.

Experimental Section

Preparation of PMNCF: PS (homopolymer, $M_w = 220000$, Beijing Yanshan Petrochemical Co., Ltd.) was dissolved in DMF (Beijing Yili Fine Chemical Co.) by stirring for 5 h to form a 7 wt % transparent solution. About 2 mL of the precursor solution was placed in a 5-mL syringe equipped with a blunt metal needle of 0.6 mm inner diameter. The syringe was placed in a syringe pump that maintained a solution feed rate of 0.5 mL h^{-1} . A stainless steel plate covered with a sheet of aluminum foil was employed as the collector. The distance between the needle tip and collector was 14 cm, and the voltage was set at 14 kV.

Preparations of films I and II were similar to that of PMNCF. A 25 wt % solution (film I) and a 5 wt % solution (film II) with feed

rates of 2 and 0.5 mL h⁻¹, respectively, were processed at the same voltage and distance as PMNCF. The native PS film was prepared from a 20 wt % PS/DMF solution by spin coating on a cleaned silicon wafer.

FE-SEM images were obtained on a JEOL JSM-6700F (Japan) scanning electron microscope at 3.0 kV. Contact angles were measured on an OCA20 contact-angle system (Dataphysics Co., Germany) at ambient temperature.

Received: April 15, 2004 [Z460333]

Keywords: electrohydrodynamics · hydrophobic effect · nanostructures · polymers · surface chemistry

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