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Super-hydrophobic coatings based on non-solvent induced phase separation during electro-spraying

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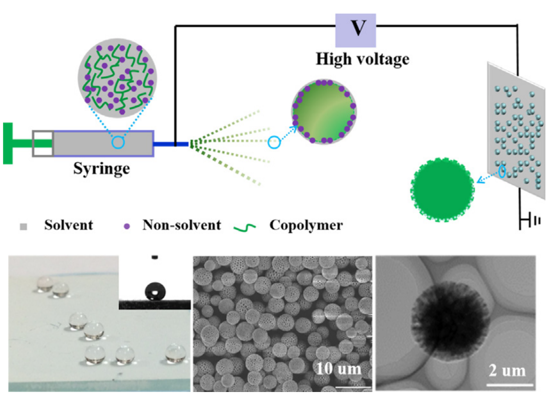
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: The polymer solution concentration determines whether electrospinning or electro-spraying occurs, while the addition of the non-solvent into the polymer solution strongly influences the surface morphology of the obtained products. Both smooth and porous surfaces of the electro-sprayed microspheres can be harvested by choosing different non-solvent and its amount as well as incorporating polymeric additives.

Experiments: The influences of the solution concentration, weight ratio between the non-solvent and the copolymer, and the polymeric additives on the surface morphology and the wettability of the electro-sprayed products were systematically studied.

Findings: Surface pores and/or asperities on the microsphere surface were mainly caused by the non-solvent induced phase separation (NIPS) and subsequent evaporation of the non-solvent during electro-spraying. With increasing polymer solution concentration, the microsphere was gradually changed to the bead-on-string geometry and finally to a nanofiber form, leading to a sustained decrease of the contact angle (CA). It was found that the substrate coatings derived from the microspheres possessing hierarchical surface pores or dense asperities had high surface roughness and super-hydrophobicity with CAs larger than 150° while sliding angles smaller than 10°; but coatings composed of microspheres with smooth surfaces gave relatively low CAs.

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1. Introduction

The wettability of a solid surface is a very important aspect of material properties since it can determine the practical applications of materials in many fields. Surface wettability is generally governed by two main parameters, i.e., chemical composition and geometrical architecture. Materials possessing a low surface free energy tend to exhibit hydrophobic performance. The surface with a water contact angle (CA) higher than 150° is called a super-hydrophobic surface. Water droplets on a super-hydrophobic surface easily roll off even at inclinations of only a few degrees, and thus surface contaminants can be easily removed. The unique water repellent and self-cleaning properties have attracted considerable interest from both industry and academia due to their potential applications as stain-resistant fabrics, self-cleaning and water-oil separation surfaces [1–5]. However, the maximum contact angle for a smooth surface is reported as only ~120° [6]. Hence, rough surface with a hierarchical micro/nano structure is designed to achieve super-hydrophobicity. Surface roughness has a great influence on the apparent contact angle θ^*, which was investigated by Wenzel [7,8] and Cassie and Baxter [9]. In Wenzel's model, the water droplet not only covers the surface asperities but also penetrates into the surface cavities, leading to an increase in actual contact area. Wenzel introduced a roughness factor *r*, which is the ratio of the actual contact area to the projected surface area, to describe the relationship between θ^* (apparent CA) and θ (CA on a flat surface), i.e., $\cos\theta^* = r\cos\theta$. In this case, the wettability is magnified, which results in a large difference between the advancing and the receding contact angles, *viz*., hysteresis. In the model of Cassie-Baxter, the liquid does not completely wet the surface contours but it is instead suspended on the asperities composed of both solid and air patches. In this case, the apparent liquid contact angle θ^* is described by:

$$\cos\theta^* = f_1\cos\theta - f_2 \tag{1}$$

where f_1 and f_2 are fractions of solid surface and air in contact with the liquid, respectively. Note that $f_1 + f_2 = 1$, it can be concluded that a larger f_2 (more air pockets) will induce a larger θ^*. The Cassie-Baxter state corresponds to a low threshold sliding angle, and thus hysteresis, because water can easily slide or roll off when it is partly located in air (CA of water in air is regarded as 180°). Hence, the Cassie-Baxter state is more desirable for real applications.

To-date, much work has been conducted to develop hierarchical micro/nano materials to achieve super-hydrophobic surfaces [10–12]. Polymer or inorganic colloid particulate coatings are a popular route to obtain a rough surface by spherical protrusions [13–16], rendering an enhanced hydrophobic surface. Here, the particles are randomly stacked on a substrate but the roughness obtained is not sufficient to acquire super-hydrophobicity. These particles are often coated with a thin layer of hydrophobic fluoropolymer to decrease the surface free energy [17,18]. Moreover, raspberry-like particles have been developed for fabrication of super-hydrophobic surfaces, in which nano-sized guest particles are decorated onto much larger host particles [19–22].

The hierarchical rough surface contributes to the dramatic increase of hydrophobicity. However, preparation of the hierarchical micro/nano particles with large surface roughness is usually a complicated and multi-step process. For example, the primary particles should be first chemically modified before layer by layer coating or growth of secondary particles. Moreover, the particles are especially difficult to transfer onto the substrates. Hence, it is critical to develop a simple but versatile method for the preparation of hierarchical rough particles. Electro-spraying technique has been proven a flexible and effective method for obtaining microscale to nanoscale particles from a range of materials, e.g., polymers [23–25], inorganic [26] and hybrid compounds [27–29]. Jiang et al. fabricated porous microspheres by electro-spraying a polystyrene (PS)/dimethyl form amide (DMF) solution [15]. Vapor induced phase separation was responsible for the formation of the porous structure and thus the rough surface, which contributed to super-hydrophobicity. It was found that the morphologies of electro-sprayed products could be tuned by adjusting the concentration of the polymer solution [15]. Clearly, hierarchically porous structure is desirable for the enhanced surface roughness and hence the super-hydrophobicity. Although porous PS microspheres were easily produced by electro-spraying, most of the electro-sprayed polymer microspheres were solid and irregular, corresponding to a low super-hydrophobicity. Therefore, it is of high importance to develop a common method for preparation of uniform and porous microspheres by electro-spraying.

In our previous work, a facile approach, i.e., non-solvent assisted electro-spraying, was used to prepare hierarchically porous PMMA microspheres for a super-hydrophobic coating [30]. Non-solvent induced phase separation (NIPS) was widely used to prepare asymmetric membranes, but was seldom explored in the electro-spraying or electrospinning. The non-solvent in the solution not only created pores, but also stabilized the droplet during electro-spraying, finally leading to the formation of regular and uniform pores. Even though the CA of the porous PMMA microsphere coating could reach 152°, the sliding angle (SA) was relatively large (>10°). To further improve the CA and decrease the SA, a copolymer, i.e., PS-PMMA, was used in this study since PS has a lower surface energy than PMMA. Also, compared to PMMA, porous structure for PS could be formed easily during electro-spraying. Thus, regular and uniform PS-PMMA copolymer microspheres with hierarchically porous structure were produced using the non-solvent assisted electro-spraying, and the copolymer microspheres based coating had a very high CA of 162° and an extremely low SA of almost zero degree, which possessed a good self-cleaning performance. The morphology evolution from porous microspheres to nanofibers, control of surface microstructure and influence on the super-hydrophobicity was systematically investigated, which could provide new insight in colloid and interface science. This non-solvent assisted electro-spraying method provides a new avenue for processing super-hydrophobic coatings.

2. Experimental section

2.1. Materials

Poly(styrene-*co*-methyl methacrylate) (PS-PMMA) with an average Mw 100,000–150,000 and styrene ~40 mol% was obtained from Sigma-Aldrich Corp. Dichloromethane (DCM), Chloroform (CFM), *N*,*N*-dimethylformamide (DMF), ethanol, butanol, hexanol and polymethylsiloxane (PDMS) were also purchased from Sigma-Aldrich Corp and used as-received. Polyvinylpyrrolidone (PVP, Mw = 40,000) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. The solubility of different solvents to the copolymer is listed in Table S1.

2.2. Electro-spraying

A certain amount of the copolymer was dissolved in a mixture containing solvent and non-solvent, then stirred for 3 h at room temperature to obtain a stable and transparent copolymer solution. DCM, CFM and DMF were used as solvents, while ethanol, butanol and hexanol served as non-solvents. The electro-spraying or electrospinning was completed in an electrospinning unit (NEU) from Kato Tech Co., Ltd, Japan. The prepared solution was then loaded in a plastic syringe (25 mL), and pushed out from a