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# Facile preparation of hybrid microspheres for super-hydrophobic coating and oil-water separation

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## HIGHLIGHTS

- $PVDF/SiO_2$ microsphere with a hierarchical micro/nano structure was prepared.
- The sliding angle for the super-hydrophobic coating was close to zero degree.
- The super-hydrophobic coating possessed a good self-cleaning performance, water jet stability and corrosion resistance.
- The superhydrophobic coating could be used to separate the oil with the salt, acid and alkali solution.
- The flexible $PVDF/SiO_2$ membrane had a high oil water separation efficiency.

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## ABSTRACT

Super-hydrophobic materials have recently attracted great interest from both academia and industry, due to their promising applications in self-cleaning, oil-water separation, etc. Here, we developed a facile one step method to prepare the hybrid polyvinylidene fluoride (PVDF)/$SiO_2$ microspheres based on electro-spraying for super-hydrophobic coating. By controlling nanoparticle concentration, the $SiO_2$ could be uniformly distributed on PVDF microsphere surface, forming a hierarchical micro/nano structure. The contact angle (CA) of the super-hydrophobic coating could reach as high as 162°, and the sliding angle (SA) could be close to zero degree. The super-hydrophobic coating possessed a good self-cleaning performance, water jet stability and corrosion resistance. It was found that gravity driven oil-water separation was achieved by using the filter paper coated with the super-hydrophobic hybrid microspheres. More importantly, the coated filter paper could not only separate the oil with the pure water but also the corrosive solution including the salt, acid and alkali solution. With the increase of the solution concentration, the free-standing membrane composed of the hybrid microspheres and ultrathin threads were obtained, and the membrane showed a high flux and efficiency for oil-water separation. In addition, the flexible membrane could be used for adsorption of different kinds of oil.



## 1. Introduction

Super-hydrophobicity, defined as the water contact angle larger than 150° while the sliding angle lower than 8°, have attracted great interest from both academia and industry, because super-hydrophobic materials have promising applications in self-cleaning, oil-water separation, etc. [1–6]. Generally, the surface wettability of materials is controlled by two main factors, namely the chemical composition determining surface energy and the geometrical architecture determining surface roughness [7–9]. Usually, material with a low surface energy displays a hydrophobic behavior; however, the maximum contact angle for a uorinated smooth surface with an extremely low surface energy is reported only about 120° that is far from super-hydrophobic [10].

In fact, super-hydrophobicity, i.e., a high contact angle and low sliding angle, has been found in insect legs and plant leaves such as lotus and silver ragwort, which usually possess hierarchical microstructures and thus high surface roughness [11]. Based on the Cassie Baxter theory, the water is just suspended on rather than diffuse into the asperities consisting of both solid and air

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patches, and hence cannot completely wet the surface contours. As a result, the hydrophobicity is improved significantly, because the contact angle for air is regarded as 180° [12].

Up to now, many methods such as template [13–16], photolithography [17], plasma treatment [18] and layer by layer deposition [19] have been developed to construct the hierarchical microstructures, amount which colloid assembly is a simple, straightforward and cost-effective way for preparation of super-hydrophobic coating [20–24]. The particle assemblies including polymer particles (e.g., polystyrene (PS) beads) and inorganic spheres (e.g., silica particles) could render roughness to the underlying substrates by the spherical protrusion, improving the surface roughness and thus hydrophobicity. However, the roughness originated from the particle stacking is usually not enough for achieving the super-hydrophobicity. These particles are often coated with a thin layer of hydrophobic fluoropolymer to decrease the surface free energy [25,26]. Zhang, et al. fabricated super-hydrophobic cotton fabrics, whose surface was prepared by utilizing cationic poly (dimethyldiallylammonium chloride) and silica particles together with subsequent modification of (heptadecafluoro-1,1,2,2-tetrade cyl trimethoxysilane) [20]. Also, strawberry or raspberry-like particles are developed for fabrication of super-hydrophobic coating, in which the nano-sized guest particles were decorated onto much larger host particles [27–30]. For example, the raspberry-like hybrid particles ($PS/SiO_2$) could be prepared for super-hydrophobic coating by combination of seeded dispersion polymerization and hydrolysis of tetraethoxysilane [28].

As mentioned above, the hydrophobicity was significantly enhanced by the rough surface from colloid particles self-assembly. Nevertheless, most of fabricating methods of the hierarchical micro/nano particles are usually complicated, and multistep manipulation is generally required. For instance, chemical modification is necessary for the primary particles prior to the following layer by layer coating or secondary particle growth. Moreover, it is difficult to transfer the particles to the target substrates. Therefore, it is of high importance to explore a simple but versatile method to prepared particles with a hierarchical microstructure. Electro-spraying technique has been recently developed to obtain either polymer [31–35] or inorganic [36,37] particles. Jiang and coworkers fabricated porous microspheres by electro-spraying PS/dimethylformamide (DMF) solution. Vapor induced phase separation (VIPS) was responsible for the formation of the porous structure and thus the rough surface, which contributed to the super-hydrophobicity [38]. Note that, the solvent used should be miscible with the water; additionally, VIPS often occurred at a relatively high humidity. To decrease the dependence of the porous structure on the solvent and humidity, in our previous work, non-solvent assisted electro-spraying was used for preparation of hierarchically porous poly(methyl methacrylate) (PMMA) microsphere, and the multi-sized surface pores mainly resulting from the non-solvent induced phase separation contributed to the super-hydrophobic coating [39,40]. Although the contact angle could reach as high as 153°, the sliding angle was relatively large, indicating the contact angle hysteresis. More importantly, both PS and PMMA that are most frequently used in elector-spinning or electro-praying for preparation of porous fibers or microspheres [41–43] are low oil resistance, and they are easily dissolved in some oily solvent (e.g., chloroform and toluene), which greatly limits their practical applications such as oil-water separation.

In this study, the hydrophobic $SiO_2$ nanoparticles with good dispersity in organic solvent was incorporated in the polyvinylidene fluoride (PVDF) solution for electro-spraying, and the hybrid $SiO_2$/PVDF microspheres with a hierarchical microstructure, i.e., nano-sized $SiO_2$ distributed on the surface of micro-sized PVDF microspheres, were finally obtained by adjusting $SiO_2$ concentration in the polymer solution. PVDF was chosen because of its extremely low surface energy and excellent chemical resistance [44,45]. A large number of asperities were produced on the surface of PVDF microspheres, due to the assembly of $SiO_2$ nanoparticles during electro-spraying, which could not only increase the contact angle but also decrease the sliding angle. It was found super-hydrophobicity in a wide pH value from 1 to 14 could be achieved for the hybrid microsphere coated substrate. The contact angle can reach as high as 162°, while the sliding angle was able to decrease to almost zero degree. Moreover, the hybrid microsphere coated filter paper could be used for oil-water separation, displaying good recycling performance. The free-standing membrane composed of hybrid microspheres together with many ultrathin threads was obtained with increase of the PVDF concentration to 20 wt%, and the membrane possessed a high adsorption capacity to different kinds of oil. This one step fabrication of the organic/inorganic hybrid microspheres and flexible membrane with multi-scale architecture provides a new venue for super-hydrophobic coating and its application in oil-water separation under harsh environment.

## 2. Experimental section

### 2.1. Materials

Poly(vinylidene fluoride) (PVDF), a commercial product, was provided by 3F New Materials Co. Ltd, Shanghai (Kynar 740). Dimethylformamide (DMF) was purchased from Sigma-Aldrich Corp. Hydrophobic $SiO_2$ nanoparticles (H15, diameter of 16–20 nm) were obtained from Wacker Chemie Company (Germany). All materials were used as received and without further purification.

### 2.2. Preparation of hybrid PVDF/$SiO_2$ microspheres

For the preparation of electro-spraying precursor solution, a certain amount of PVDF pellets was dissolved in DMF, followed by addition of $SiO_2$ nanoparticles. The mixture experienced ultra-sonication for 5 min, which was subsequently subject to magnetic stirring at 60 °C for 6 h. The stable and homogeneous solution mixture was then loaded in a syringe connected with a metallic needle for electro-spraying. The solution mixture with the same $SiO_2$ concentration was casted for preparation of the hybrid membrane, whose hydrophobic performance was compared with that of substrate with hybrid microsphere coating. For convenience of description, PSi-X and PSi-CX are used to represent the hybrid PVDF/$SiO_2$ microspheres and casting membrane where X and CX refers to the $SiO_2$ concentration (weight percentage) in the electro-spraying solution and casting solution, respectively. The electro-sprayed products were collected in a grounded aluminum foil, which was 12 cm far from the metallic needle. Unless otherwise specified, the parameters for electro-spraying were chosen as follows: PVDF concentration: 4 wt%; the voltage: 12 kV; the flowing rate: 1 mL $h^{-1}$.

### 2.3. Morphology characterization

The morphologies of the electro-sprayed hybrid microspheres were characterized using a Supra 55 field emission scanning electron microscope (FE-SEM, Zeiss Concept, Germany) operating at 5 kV. The electro-sprayed hybrid microspheres were also deposited on copper grids covered with a carbon film for Transmission Electron Microscopy (TEM) observation, and the accelerating voltage was 20 kV. The size distribution of the hybrid micropsheres was analyzed from the SEM images using the software of Nano measure. The average surface roughness (Ra) of the