BIOMIMETIC MICROSPHERES WITH ROUGH STRUCTURE BY THE GEOMETRIC POTENTIAL THEORY

by

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Rough structure microspheres developed using electrospinning show many superior properties, such as increased specific surface area and enhanced wettability, yielding numerous benefits to the applications in adsorption, separation, and others. In this study, biomimetic rough microspheres on string of polymethyl methacrylate nanofiber with hierarchical structure of micron-scale microsphere, and nanoscale Y-shape edges on the microsphere were innovatively and successfully developed by electrospinning. The resulting microsphere exhibited a steering-wheel-like Y shape, and the formation process was physically explained by the geometric potential theory. In the spinning process, irregular hexahedron-like droplet was firstly formed. Then, the hexahedron-like droplet changed to tetrahedron-like after the bottom contacted the collector. The tetrahedron-like droplet evolved into Y-shaped microsphere due to the geometric potential and the collapse of the center part owing to the solvent evaporation. Furthermore, similar to the natural lotus leaf, the hierarchical steering-wheel structure strengthened the nanofiber membrane roughness and endowed the membrane with superhydrophobicity, indicating the potential application in water treatment (oil-water separation, and dye and heavy metal ion adsorption), functional surface materials (self-cleaning fabrics), energy generation and other salient areas.

Key words*: biomimetic, geometric potential, hierarchical, microsphere, superhydrophobicity, oil water separation*

Introduction

Special surface materials can be found in nature such as lotus leaf [1], silver ragwort leaf [2], rose petals [3] and others. Inspired by the nature, special wettability materials, including superhydrophobicity, superhydrophilicity, switchable superhydrophobicity and superhydrophilicity, have been fabricated by academic and industrial researches [4-6]. Therein, superhydrophobic materials show promising applications in self-cleaning, anti-corrosion and energy generation [7, 8]. To date, various methods have been developed to construct superhydrophobic materials such as layer-by-layer method [9], electrochemical deposition [10], chemical vapor deposition [11], template [12] and electrospinning [13].

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Among them, electrospinning technology shows superior advantages of one-step forming process, controllable membrane parameters and robust superhydrophobicity [14, 15]. To construct superhydrophobic surface, two strategies of increasing roughness on surface with low energy, and coating low energy matters on rough surface have been intensively developed [16-18]. Ever since Jiang *et al*. [19] reported that beaded polystyrene by electrospinning exhibited superhydrophobicity due to its roughness, many literatures on the creation superhydrophobic materials using electrospun microsphere have been published. For example, Gao *et al*. [20] developed microspheres with rough and smooth surfaces using the non-solvent additive electro-spraying. The resulting microspheres with rough surface showed larger than 150° water contact angle (CA) while the microspheres with smooth surface gave relatively low water CA. Gao *et al*. [21] reported that microspheres could enhance the electrospun membrane roughness and endow superhydrophobicity to the membrane. Lee *et al*. [22] prepared aerogel-assisted microsphere-coated electrospun membrane with water CA of 162.1°. These reports clearly demonstrate the benefits of increased water CA by microspheres.

However, although these microspheres increase the surface roughness and endow superhydrophobicity, special shaped microspheres, such as the steering-wheel-like microsphere, and their formation mechanism via the geometric potential theory have been rarely reported.

The geometric potential theory explains that a surface can form a force [23]. For example, the boundary-induced force (the geometric potential) pushes the water upwards after a capillary is immersed into water [24]. In the dry spinning process, the circular boundary of the moving jet due to the circular nozzle produces a force towards the jet center and finally forms a cylindrical fiber [25]. Similarly, for a square nozzle, the square boundary produces a perpendicular force to each side of the boundary, resulting in an X-shaped fiber [25]. Therefore, the geometric potential can well explain the phenomenon in nature and social life. However, the geometric potential associated with microsphere, such as the steering-wheel microsphere, has yet to be reported and should be further developed.

In the present study, we developed steering-wheel-like microsphere on a string of polymethyl methacrylate (PMMA) nanofiber by electrospinning. The resulting steering-wheel like microsphere possessed hierarchical structure with microsphere (micron-scale) and edges of Y (nanoscale) on the microsphere, which was similar to the natural lotus leaf structure where the submicron/nanometer bumped on the surface of micron bumps. The related formation mechanism was tentatively explained by the geometric potential theory. Moreover, the wettability of the resulting membrane was characterized and the proper mechanism of the superhydrophobicity was expounded.

Experimental

Materials

Polymethyl methacrylate, M_w = 350000 gmol^{-1}, was purchased from Aladdin Industrial Corporation, Shanghai, China. Acetone was supplied by Sinopharm Chemical Reagent Co. Ltd. (Suzhou, China). All reagents were analytical grade and were used as received without further treatment.

Preparation of PMMA microspheres by electrospinning

The PMMA solution with concentration of 12 wt.% was obtained by stirring the PMMA and acetone for 6 hours at room temperature. In the spinning process, the voltage supply was 15 kV, the collector distance was 12 cm, the solution flow rate was 0.8 mL per hours, and the relative humidity was kept at 5 ±2% in a sealed home-made box using desiccants.

Results and discussion

The morphology of steering-wheel like microsphere by electrospinning

Microspheres with rough surface structure can be developed by electrospinning method. Microspheres with pore on the surface are usually obtained [26, 27]. However, the microsphere with Y-shaped-like structure has rarely been reported. As shown in figs. 1(a), and 1(b), the PMMA nanofibers with beads on string structure were achieved. Interestingly, the extremely wrinkle structure appeared on the microspheres. The wrinkles showed the Y-shaped structure with the edge diameter of about 250 nm, making the microsphere to be like a steering wheel. The hierarchical structure with microsphere (micron-scale) and edges of Y (nano-scale), fig. 1(c) was similar to a natural lotus leaf structure where the submicron/nanometer bumped on the surface of micron bumps, figs. 1(e) and 1(f), [28]. This hierarchical structure resembled lotus leaf and other natural materials, such as rose leaf and silver ragwort leaf, efficiently enhanced the nanofiber membrane roughness, and strengthened the membrane hydrophobicity.

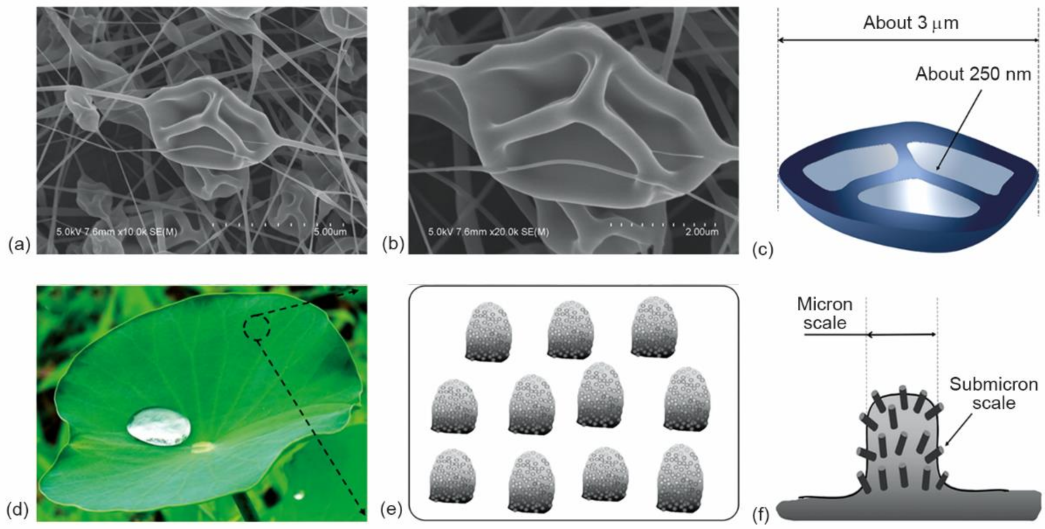

Figure 1. The morphology of electrospun steering-wheel-like microsphere and lotus leaf; (a) the steering-wheel-like microsphere × 10,000, (b) the steering-wheel-like microsphere × 20,000, (c) the size of the steering-wheel-like microsphere, (d) the optical image of the lotus leaf, (e) the schematic diagram of the pumps on the lotus leaf surface, and (f) the size of the pump on the lotus leaf surface

The forming mechanism of the hierarchical steering-wheel-like structure can be explained by the geometric potential theory. Figure 2 is the schematic diagram of the evaluation of the steering-wheel-like microsphere. In the spinning process, an irregular hexahedron-like droplet was formed during the charged jet moving in the air, fig. 2(a). After the droplet contacted the collector, the bottom of the droplet flattened and the top of the droplet became trihedron-like structure, fig. 2(b). After that, the trihedron-like structure began to sink due to the geometric potential, fig. 2(c). Then, it continued to sink until becoming almost flat gradually, fig. 2(d). After that, the Y-shape was formed due to the collapse of the center part because of the continued sinking of the geometric potential and simultaneous solvent evaporation, fig. 2(e). Then, the microsphere with steering-wheel-like structure was successfully developed. The part surrounded by the dotted green line was the evolution of one of the faces of the trihedron-like structure, fig. 2.

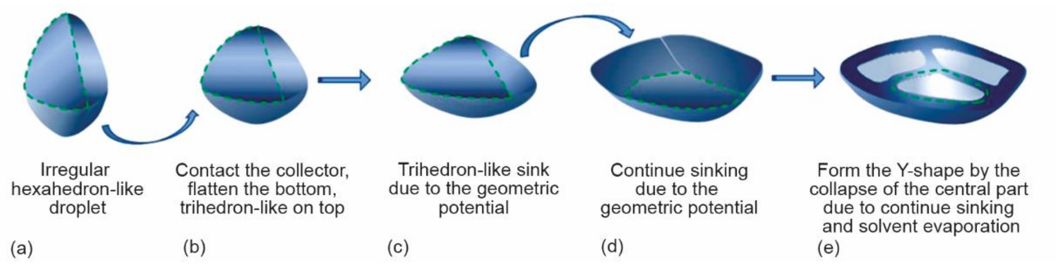

Figure 2. The schematic diagram of the evolution of the steering-wheel-like microsphere

The formation process of the steering-wheel-like microsphere can be further explained by fig. 3. As shown in fig. 3(a), each of the triangular face (marked by the green line) had the tendency (marked by the red arrow) to sink due to the geometric potential. After the droplet touched the bottom, the triangular face of the trihedron-like structure on top kept sinking by the geometric potential, figs. 3(a) and 3(c). Meanwhile, each edge of the triangular face had the tendency, marked by the red arrow, fig. 3(c), to sink and subsequently, to form three flat triangular-like structure due to the continued sinking by the geometric potential, fig. 3(d). Then, the holes were formed due to the collapse of the triangular center part and to the continued sinking and solvent evaporation. Meanwhile, the edges of the triangles were further highlighted, presenting a Y-shape on the microsphere, fig. 3(e). Finally, the Y-shaped, steering-wheel-like microsphere was successfully developed.

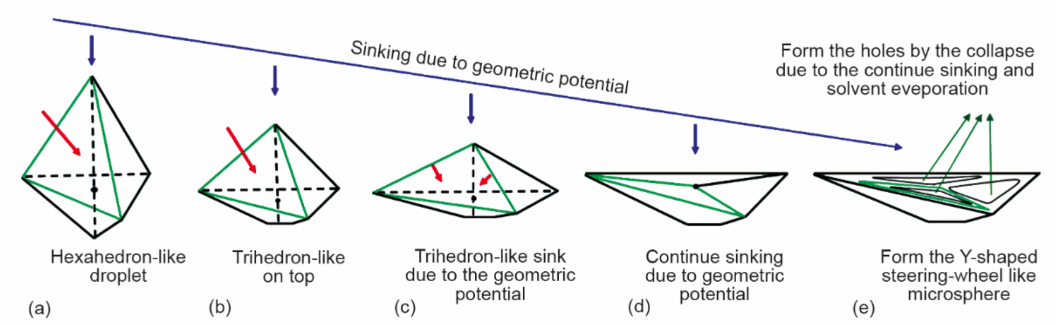

Figure 3. The schematic diagram of the evolution of the steering-wheel-like microsphere

The Cassie and Baxter law [29] describes that the rougher the surface of the hydrophobic material, the stronger the hydrophobicity. The natural lotus leaf possesses the structure of submicron/nanometer bumps on the surface of micron bumps, endowing superhydophobi-

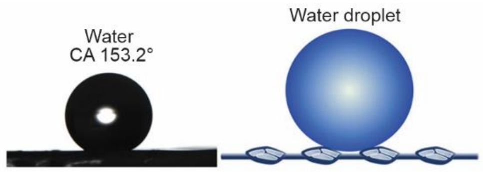

Figure 4. The wettability of the membrane with steering-wheel like structure; (a) the water contact angle and (b) the schematic diagram of the superhydrophobicity mechanism

city to the lotus leaf due to the increased surface roughness. Similar to natural lotus leaf, the resulting steering-wheel-like microsphere presented a hierarchical structure and significantly enhanced the nanofibrous membrane roughness, suggesting its superhydrophobicity. The special wettability was demonstrated by the result of water CA of 153.2°, fig. 4(a). The Y-shape structure on the microsphere can increase the air captured by the membrane [30]. As a result, hydrophobicity was strengthened by the increased air between the water droplet and the membrane interface, fig. 4(b).

The nanofibber surface morphology is controlled by the fractal Bratu-type equation [31], by suitable control of the spinning process and the receipt system, the hydrophobicity can be converted to hydrophilicity [32], the bubble electrospinning can control the nanoscale surface morphology easily [33, 34]. Peng and He [35] explained the amazing phenomenon by the geometrical potential theory, and Tian' *et al.* [36] concluded the selective adsorption property for a nanoscale surface. The nano/micro scale surface morphology has high surface energy (geometrical potential), so it can be used for energy harvesting [37, 38] and moisture harvesting [39, 40], and anti-fouling [41].

Conclusion

In conclusion, biomimetic steering-wheel-like microsphere, with hierarchical structure of micron-scale microsphere and nano-scale Y-shape edges on the microsphere, was successfully developed. The formation mechanism was physically explained by the geometric potential theory, whereby the tetrahedron-like droplet continued to sink and to evolve into Y-shape microsphere due to the geometric potential and the collapse process by the solvent evaporation. Furthermore, the Y-shape structure effectively enhanced the membrane roughness and endowed superhydrophobicity to the nanofibrous membrane. Therefore, this study provides an approach to construct microsphere with peculiar structure and functional property, drawing attention to them, and benefitting the applications in terms of surface functional treatment, water treatment, and many other related areas.

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