3D Printed and Plasma Treated Superhydrophobic Mesh Filters for Oil-Water Separation

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ABSTRACT

A potential advantage of three dimensional printing (3DP) is fabricating complex structures with reduced manufacturing time and procedures. The goal in this study is to create mesh filters with various pore sizes and wetting properties for oil-water separation. We made mesh filters with the 3DP and applied plasma treatment using a radio-frequency plasma-enhanced chemical vapor deposition (rf-PECVD) to control their surface wettability and geometry. The created nanohair structures on the mesh surfaces were further coated by hexamethyldisiloxane (HMDSO) to convert the surface wetting property. The efficiency of the oil/-water separation function was evaluated by observing the behaviour of oil-water mixture droplets on the functionalized mesh filters. The HMDSO coated mesh filters exhibited sufficient superhydrophobic and superoleophilic properties resulting in excellent oil separation capability from the oil-water mixture. Furthermore, we demonstrated that filtration of mixtures through the mesh filters was influenced by mesh pore sizes directly. The combination of 3DP technique and plasma treatment by PECVD makes very promising mesh filters for practical applications like oil spill cleanup or separation.

Keywords: three dimensional printing, oil-water separation, radio-frequency plasma-enhanced chemical vapor deposition, superhydrophobic surface, filter

1 INTRODUCTION

As environmental concerns are increasing, the threat of water pollution by oil contamination has prompted the desire for clean water purification system. Due to the rapid development of global industry and frequent trade, oil-spill accident into water always opens and causes the negative environmental impacts by leading directly lack of clean and fresh water. As a result, growing demand has been sparked in developing effective filter types for oil-water separation, oil spill cleanup, decontamination of water, etc. Currently, one of the common water treatment methods is oil-water separation through filters. Diverse approaches have been employed for the fabrication of functional filters involving self-assembly, electrospinning, and lithography [1-3]. However, there are a lot of challenges for large-scale fabrication with complicated porous shapes and sizes, which accompanies expensive fabrication process, difficult selectivity and modification, uncontrolled reaction in bulky condition [4]. In light of these emerging limitations, it is required to develop simple and precise methods for the fabrication of excellent filter structures to apply into macroscopic devices.

In contrast to the aforementioned approaches, the 3DP method can be a powerful way to make mesh filters not only giving controlled pore shapes and sizes with extremely simple fabrication process but also producing mass produced or differently customized types simultaneously. The shapes are generated directly from computer aided design (CAD) files and constructed by slicing the 3D CAD models with cross-sectional data. The 3DP uses standard inkjet printing technology to arrange and stack up the desired geometry by starting from small building powders. Evenly distributed powder is based and a print head moves onto the thin layer of powder following the sliced profile of the computer model. A liquid binder is ejected from the printer head to join adjacent powders and create parts layer-by-layer. The subsequent stacking and printing of powder layers forms the complete structure of the desired 3D object eventually.

Here, we fabricated differnt sized mesh filters with the 3DP and applied them for oil-water separation. It is well known that wettability of surface is generally governed by change in surface roughness and topography [5]. According to the Wenzel and the Cassie–Baxter model [6, 7], the surface topography could either enhance or reduce wetting more, depending on the introduction of a proper micro- or nanostructures. A superhydrophobic surface which has high water contact angle (>150°) is generally oleophilic or superoleophilic. Therefore, the controlling surface wettability on the filter plays an essential role in the effective oil-water separation. For surface modification, plasma technology has received great attraction because plasma processing can be used in generation of both morphological roughness and chemical coating [8, 9]. It is being utilized to improve surface properties by applying reactive gas plasma such as oxygen (O_2) to the surfaces. The plasma treatment has many advantages including a dry and precise technique, eco-friendly technique, low cost, and high productivity via simple processes [8]. Coupled to this, oil-water separation procedures were performed by three procedures in this study: (1) mesh filters fabrication with the 3DP, (2) plasma etching and coating on the mesh filters and (3) oil-water separation tests.

2 EXPERIMENTAL SECTION

2.1 Fabrication of mesh filters with the 3DP method

A commercial 3DP (Projet 160, 3D Systems) was used in all printing experiments. Meshes with different pore sizes were designed using 3D CAD software. Each sliced layers were built layer by layer with the layer thickness of about 100 µm. When the 3DP process completed, unbound and excess powder was blown away by using an air gun. The whole mesh dimension was 5 × 5 (cm), thickness was 1 mm, and the mesh gap between the pores was 1 mm, respectively (Fig. 1). Cuboid pore shapes were fabricated with various pore sizes as 1, 1.5, and 2 mm, respectively. The printed mesh filters were infiltrated with a curable monomer (Axia instant glue, Alteco, Korea) as post-treatment. This liquid comprising of cyanoacrylate monomers rapidly polymerized to solid polycyanoacrylate on the surface to be bonded.

2.2 Preparation of the superhydrophilic and superhydrophoic mesh filters

The oxygen plasma etching technique using the rf-PECVD system was employed to fabricate micro- and nanostructures on the surfaces of the printed mesh filters. The constructed meshes were introduced in a custom built reaction chamber and etched by O_2 gas. The plasma etching was performed by the duration of 5 min and 30 min under the bias voltage of 400 V and the gas pressure of 20 mTorr. The treated meshes were subsequently coated by HMDSO for 30 sec to create hydrophobic surfaces. At this process, the gas pressure and the bias voltage were maintained at 10 mTorr and 400 V.

2.3 Characterization

The morphologies of the mesh surfaces were observed before and after the plasma treatment using a field emission scanning electron microscope (FE-SEM, Nova NanoSEM 200) operated at 10 kV. Before the SEM observation, all samples were fixed on aluminium stubs and coated with platinum. Contact angles were measured under ambient condition using a Goniometer. Water droplet (10 µl) was dropped carefully onto the mesh surface.

2.4 Oil-Water separation experiments with the 3D printed mesh filters

For the oil-water separation, the as-prepared mesh filter was placed between two glass slides and checked filter capability. A mixture of silicone oil colored with sudan blue II and water colored with red stamp ink was dropped slowly on the mesh filters. To investigate water and oil behaviour separately, each solution was also dropped on the same mesh. The droplet motion was recorded by a digital camera (Canon) to see separation efficiency.

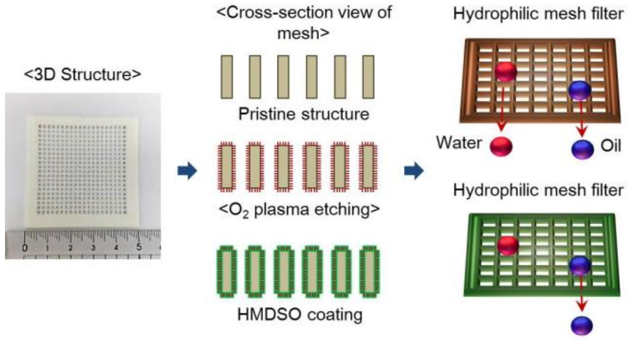

Figure 1: Schematic diagram of mesh filter preparation procedures.

3 RESULTS AND DISCUSSION

3.1 Surface treatment of the 3D printed mesh filters

Figure 2 shows SEM images of the mesh filters before and after the surface plasma treatment. The surface of pristine mesh (Fig. 2a) exhibited a quite smooth surface. In contrast, the meshes exposed to the O_2 plasma etching by PECVD, the surfaces became rough due to the creation of hairy-like nanostructures as shown at the highest magnification in Fig. 2b-2c. The plasma etching enables selective removal of materials from a surface by reactive plasma radicals [8]. In addition, little fluorine depletion and oxygen introduction is observed in the air plasma condition along with extensive morphological changes. Under this condition, the nanohair structures begin aggregation due to the van der Waals forces between these structures obtained after 5 min and 30 min of the plasma treatment. These results proved that O_2 plasma etching is suitable in development of micro- and nano-structured roughness on 3DP powder based materials.

However, the different etching duration generated different patterns with different aspect ratios on the mesh surfaces. From the Fig. 3 taken under the 30° titled angle, it is more clearly seen that there were a significant difference in physical dimensions. The nanohair structures forming under short etching time had shorter height (ca. 0.6 µm) while that forming under the long etching time had comparatively longer height (ca. 1.1 µm). We also carried out surface modification with plasma polymerization coating system using HMDSO after the O_2 plasma etching. The morphological change of the mesh surface was mainly caused by the bonding of activated species and depended on the plasma condition in coated processes using HMDSO[10]. The deposited thin film was approximately 50 nm in thickness and it did not alter the roughness of the O_2 plasma etched surface (not shown).

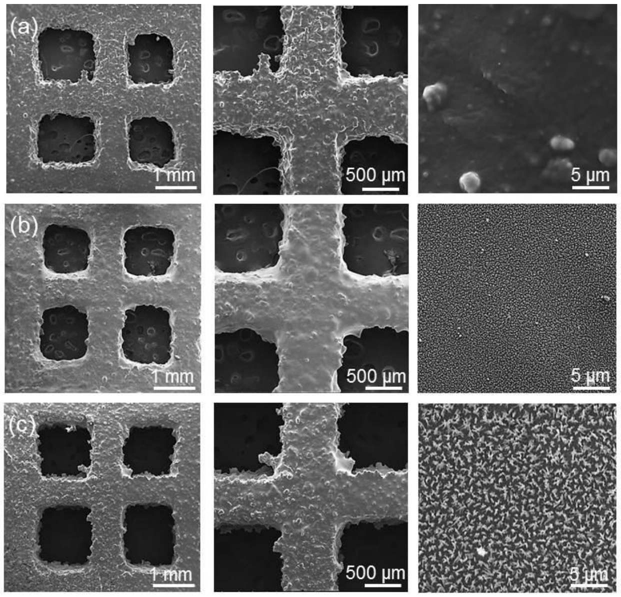

Figure 2: SEM images of (a) untreated original mesh, O_2 plasma treated mesh for (b) 5 min, and (c) 30 min. From left to right, magnification is enlarged at the center of the figure to observe the surface geometry clearly.

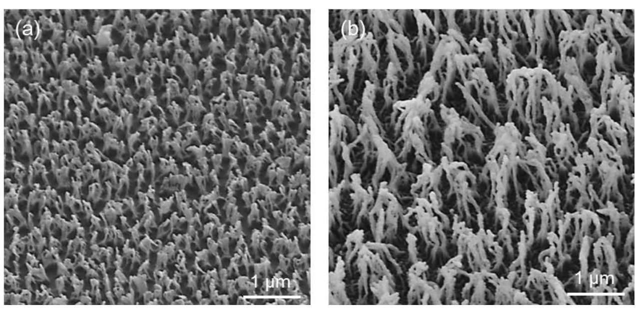

Figure 3: Tilted SEM images (30 °) of O_2 plasma treated mesh for (b) 5 min, and (c) 30 min.

3.2 Oil-Water separation

The wettability and oil-water separation properties of the as-prepared mesh filters were characterized comprehensively as presented in Fig. 4. For comparison, the untreated pristine mesh, the mesh treated by plasma etching with O_2 for 5 min and 30 min, and the coated mesh by HMDSO were utilized for the oil-water separation. The pristine mesh filters exhibited oleophilic property at all pore sizes as shown in Fig. 4a. It is clearly presented that the separated color zones were appeared as up (water) and down (oil) placement.

On the other hand, the surfaces treated by the plasma etching resulted in significant enhanced superhydrophilic and oleophilic properties (Fig. 4b-4c). The rough structures with micro/nanoscale features on the surfaces are believed to contribute to this wetting behavior. Therefore, the plasma treated mesh led to its inability to separate oil and water at the large pores (1.5 or 2 mm). As a result, water droplet was permeable through the pores as well as the silicone oil. Furthermore, we found that the oil droplets were quite unstable on the etching surfaces and they could readily penetrate via the pores suggesting a low adhesion of the surface to the oil droplet. The change of surface wettability was also demonstrated through the CA in Fig. 5b. The CA was decreased from 95.6 º to 52.2 º according to the O_2 plasma treatment and eventually reached to the CA of almost 0 º on the 30 min treated mesh filter. It means that the water immediately spread on the filter as soon as contact to the surface.

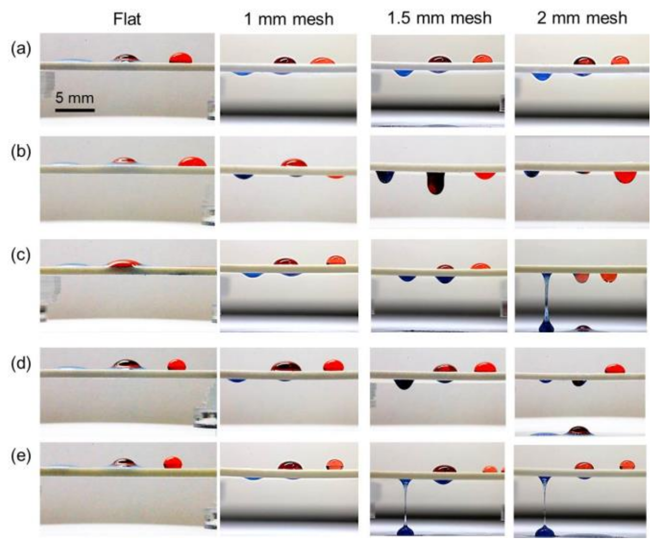

Figure 4: Oil-water separation behaviour at the different mesh filters with different pore sizes and surface functional properties. (a) Pristine, O_2 plasma etching for (b) 5 min, (c) 30 min, (d) pristine coated by HMDSO, and (e) O_2 plasma etched mesh (30 min) coated by HMDSO. Red: water, Blue: oil. The oil-water mixture was dropped at the center of each filter.

In contrast, the O_2 plasma treated surface lost superhydrophilicity once it was coated by HMDSO (Fig. 4d-4e). The water CA in this case was about 157.7 º(Fig. 5), indicating that the HMDSO coated mesh filters showed superhydrophobic and high oil-adhesion properties with the same nanostructured geometry. The oil in the mixture spread immediately on the mesh filters, quickly flowed through the pores, and dropped to the bottom. Meanwhile, the water droplet was unstable on such meshes, spontaneously bounced off, and finally was retained above the mesh because of the superhydrophobic and low water-adhesion properties of the HMDSO coating. As a result, the separation efficiency was considerably high and so no visible water existed in the permeated oil. However, the mesh filter coated by HMDSO directly without O_2 plasma etching had the CA was 139.4 º. Therefore, it confirms that the HMDSO coating itself did not make the superhydrophobic surface and so both the nanohairy-like structures and the HMDSO coating are essential to form the effective oil-water seperation filter.

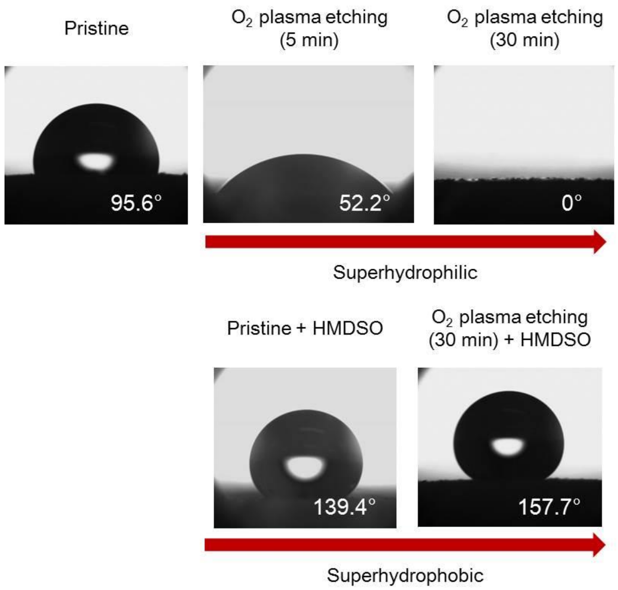

Figure 5: The static water CA on the different mesh filter.

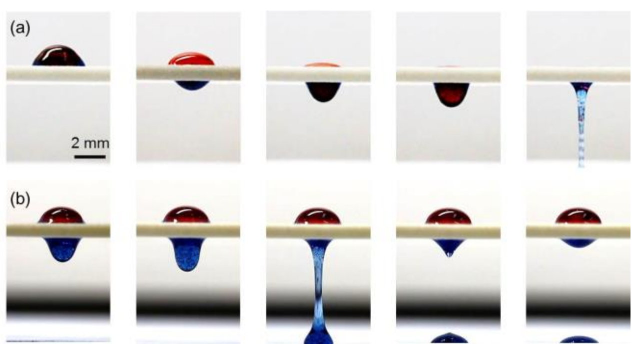

Figure 6: The dynamic motion of oil-water mixture on the (a) hydrophilic (O_2 plasma etching for 5 min) and (b) superhydrophobic mesh filter (O_2 plasma etching for 30 min with HMDSO coating). The pore size: 1.5 mm.

However, the above-mentioned all phenomenons showed different characteristics depending on the mesh pore sizes despite of the same surface condition (Fig. 4). The water droplets sit on the all mesh filters with comparatively small mesh sizes (1 mm or 1.5 mm) regardless of the surface treatment. In addition, the oil droplets slowly spread and pinned along the contacted mesh pores. Thus, oil in the mixture did not completely fall down. Additionally, water itself could not penetrate the small and middle pore sizes (1 mm or 1.5 mm) even though the surfaces were superhydrophilic, while water could pass through the large pores (2 mm). These results proved that the wettability of the mesh filter was also influenced by the pore size largely. The experimental results indicate that the optimal pore size of the mesh filter is at least 2 mm at this system. Therefore, it should be considered to design the suitable mesh filters for oil-water separation.

The different behaviour of oil-water separation shows more clearly on the hydrophilic and hydrophobic surface through the dynamic motion of oil-water mixture droplet. The evolution of length scaled roughness and HMDSO coating would greatly contribute to modify the wetting characteristics of the mesh filters.

4 CONCLUSION

In conclusion, we successfully fabricated effective functional mesh filters with unique superhydrophobic and superoleophilic properties by using the combination with the 3DP and the plasma treatment techniques. The 3DP was a superb approach to fabricate diverse mesh filters with different pore sizes in easy-to-use way and low operating time and process. The plasma treatment methods were also very useful to construct micro- or nanoscale hierarchical structured rough surfaces and to control different surface wettability. At the large mesh size, both water and oil penetrated indiscriminately through the mesh filters with the O_2 plasma treated pores. On the other hand, the meshes coated by HMDSO totally converted the surface wettablility from superhydrophilic to superhydrophobic. They could selectively separate oil from the oil-water mixture with high separation efficiency. Therefore, we proved that the plasma treatment in conjunction with 3DP fabrication technique had a significant effect on making oil-removing mesh filters. It is a good candidate for functional filtration devices in practical separation applications including industrial oil-polluted water treatments, oil spill clean-up or filters.

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