Multiscale Structures Aggregated by Imprinted Nanofibers for Functional Surfaces

Video Article

Multiscale Structures Aggregated by Imprinted Nanofibers for Functional Surfaces

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Abstract

Multiscale surface structures have attracted increasing interest owing to several potential applications in surface devices. However, an existing challenge in the field is the fabrication of hybrid micro-nano structures using a facile, cost-effective, and high-throughput method. To overcome these challenges, this paper proposes a protocol to fabricate multiscale structures using only an imprint process with an anodic aluminum oxide (AAO) filter and an evaporative self-aggregation process of nanofibers. Unlike previous attempts that have aimed to straighten nanofibers, we demonstrate a unique fabrication method for multiscale aggregated nanofibers with high aspect ratios. Furthermore, the surface morphology and wettability of these structures on various liquids were investigated to facilitate their use in multifunctional surfaces.

Video Link

The video component of this article can be found at https://www.jove.com/video/58356/

Introduction

Nanoscale textured structures such as nanoparticles, nanotubes, and nanofibers have attracted attention in the scientific community, as they demonstrate unique characteristics in various applications including electrical, biomedical, optical, and surface engineering[1,2,3,4,5,6,7,8]. In particular, nanofibers are widely used in stretchable and transparent electrodes[9], wearable sensors[10,11], interconnections[12,13], and nano-optics applications[14]. Among the various methods of fabricating nanoscale structures, such as sol-gel methods, self-assembly, lithography, and replication[15,16,17,18,19,20], direct replication using a template is currently considered a promising method because it is simple, cost-effective, and applicable to various curable materials[21,22,23,24,25,26].

Owing to its multiscale structure having a large number of nano-scale pores and micro-scale height, AAO is widely used as the template for fabrication of nanofibers and nanotubes with a high aspect ratio[27,28,29,30]. However, because of the surface tension at such a high aspect ratio, nanofibers tend to easily aggregate[31,32,33]. Existing research has proved that nanofibers having an aspect ratio greater than 15:1 do not stand upright but instead aggregate, whereas those having a ratio less than 5:1 are individually isolated without aggregation[33,34]. Capillary force and surface tension play an important role upon the removal of alumina using an etchant, which is one of the processes during nanofiber fabrication. When aspect ratio increases, surface tension among nanofibers tends to pull them closer to one another, causing aggregation. Several studies have focused on methods to prevent such aggregation[35], which is particularly observed in polymer and metallic nanofibers. Among these, hydration of the nanofiber surface may reduce the agglomeration because when a liquid occupies the spaces between nanofibers, surface tension decreases. Further, the freeze-drying method may also reduce aggregation by decreasing surface tension between nanofibers. However, despite various efforts, the straightening of nanofibers with a high aspect ratio remains a challenge.

To this end, we report a unique method for fabricating multiscale structures of tangled nanofiber by exploiting the aggregation phenomenon in a positive manner. Here, the nanofiber structure is imprinted using an AAO filter and polyurethane-acrylate (PUA)-type resins with a viscosity of 257.4 cP. After UV nano imprint lithography (UV-NIL) is performed, the mold is etched with a NaOH solution. To characterize the proposed multiscale structures, we investigate the pattern behaviors of the sample with aggregated nanofibers and the surface wettability after proper surface treatments such as coating with a self-assembled monolayer and UV ozone treatment. Furthermore, we propose that the multiscale porous surface can be converted simply to a slippery surface using a lubricant-infused process.

Protocol

1. Fabrication of Nano-Micro Multiscale Structure Surface Using an AAO Filter (Figure 1)

1. Purchase an AAO filter with a pore size, height, and diameter of 200 nm, 60 µm, and 25 mm, respectively.
2. 1.2. Clean the surface of the Polyethylene terephthalate (PET) film having a thickness of 100 µm to use acetone with 99.8% and isopropyl alcohol (IPA) with 99.9% for 5 min, and completely dry for 3 min using an air gun.
3. Place the PET film on a flat surface without contaminants, and add a 0.1 mL drop of UV-curable polyurethane-acrylate (PUA)-type resin with a viscosity of 257.4 cPs onto the surface.
4. Place the AAO filter on the resin and press uniformly, using a rubber roller with a diameter of 32 mm. The spread of the resin is visually confirmed, so the roller must be repeatedly and carefully pushed when pressing.
   CAUTION: The AAO filter is brittle and may break if excessive force is applied.
5. After rolling, expose the specimen made with the PET and AAO filter (attached using the resin) to UV light with a wavelength of 365 nm for 30 s to cure the resin.
6. Immerse the cured specimen in 100 mL of 2 M NaOH solution for 10 min to dissolve the filter.
   NOTE: The SEM images show the cross-section and surface of the structure (**Figure 2**).
7. Clean the specimen with DI water, then completely dry it for 3 min using an air gun.
   NOTE: EDX analysis confirmed that Na and Al were not detected and were completely etched (**Figure 3**).

2. Surface Treatments

1. UV ozone treatment
2. Clean the specimen with nano-micro multiscale structures using IPA and DI water for 5 min, then dry it using an air gun for 3 min.
3. Irradiate the side of the multiscale structures of the specimen (the side with multiscale structures) using UV rays (wavelength of 185-254 nm) for 60 min.
   NOTE: The UV ozone equipment has an intensity of 25 mW/cm^2.
4. Octadecyltrichlorosilane (OTS) self-assembly
5. Place a hot plate inside the glove box and maintain a N_2 environment for a vapor deposition process.
6. Fix the edge of the specimen on a glass or flat plate using adhesive tape. Ensure that the size of the glass or plate is large enough to cover the top of a beaker (with 8 mm of diameter and 13 mm of height).
7. Place the beaker on the hot plate with 5"x7" and add 2 mL of OTS solution tothe beaker using a pipette.
8. Cover the beaker with the glass or plate face-on, with the specimen facing downward into the beaker.
9. Process for 60 min at 100 °C, then remove the specimen from the glove box.
   NOTE: After the OTS-coating process, the beaker and glove box must be cleaned.

3. Fabrication of Functional Surface by Injecting Lubricants

1. Deposit approximately 0.2 mL of perfluorocarbon (PFC) liquid onto the OTS-coated self-aggregated nanofiber assembly.
2. Observe the wetting process of PFC using an optical microscope with an objective lens at 5X-20X.
3. Remove the excess PFC liquid by placing the samples in a vertical position for a few hours.

Representative Results

We demonstrated a fast and simple method for the fabrication of multiscale nano-micro hybrid structures using an AAO filter as an imprinting mold. The entire process took 30 min (**Figure 4**). It was noted that after undergoing the etching process using NaOH, the resultant surface exhibited an opaque color similar to the original AAO filter, owing to the aggregated nanofiber assembly caused by surface tension. Further, the results of the EDX analysis confirmed that the AAO filter was completely removed by wet chemical etching (**Figure 3**).

The surface characteristics were determined by measuring the contact angle by dropping onto the surface of specimen 5 µL of water droplets. Because the materials used in the AAO-filter-mediated imprint process exhibit superhydrophilicity, and the fabricated multiscale structures have highly porous networks due to self-aggregated nanofibers, the water droplets tend to be instantaneously absorbed into the substrates. However, the hydrophilicity can be modified to hydrophobicity using proper surface treatments. We demonstrated, as shown in **Figure 5**, that the surface of the imprinted multiscale structures was modified to a hydrophobic surface with a contact angle of approximately 117° after OTS coating. In addition, UV ozone treatment can further increase the contact angle of the surface by approximately 10° (**Figure 6**). After sequentially performing OTS coating and UV ozone treatment onto the imprinted surface, it was confirmed that the resulting contact angle increased to 134° (**Figure 7**).

The surface and cross-section of the specimen with OTS coating show aggregation of the nano-fibers (**Figure 5**), which results in a dimple structure. The size and orientation of this dimple structure is irregular; however, this phenomenon occurred throughout the entire surface of the specimen. The surface of the specimen became smooth after it was subjected to the UV ozone treatment process[36] (**Figure 6** and **Figure 7**). This is also why the contact angle of the surface increased after the UV ozone treatment process. This phenomenon also occurred uniformly on the surface of the specimen, and the error of the contact angle was less than 3°.

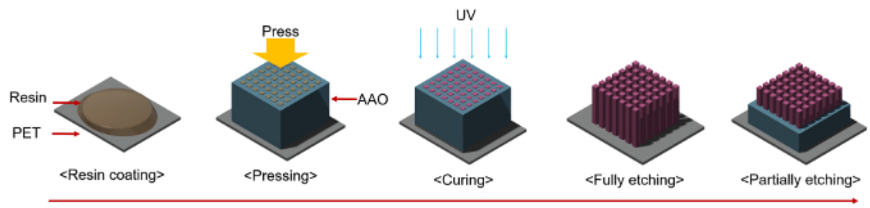

Figure 1: Procedure for fabricating a structure with soluble aluminum oxide. Please click here to view a larger version of this figure.

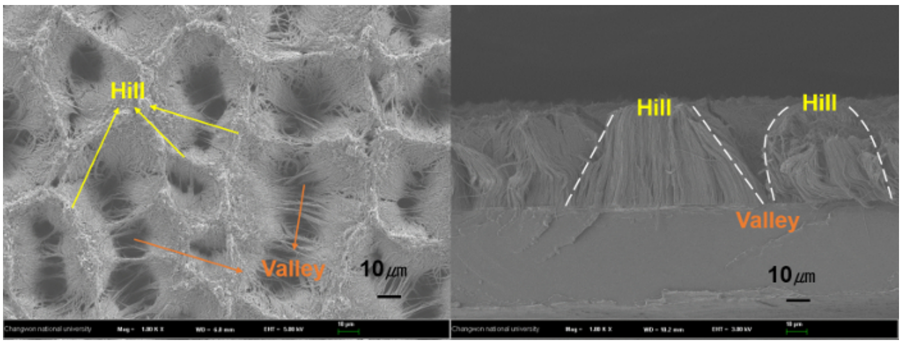

Figure 2: SEM images of a nano-micro multiscale structure after the etching process, showing the surface and cross-section. Please click here to view a larger version of this figure.

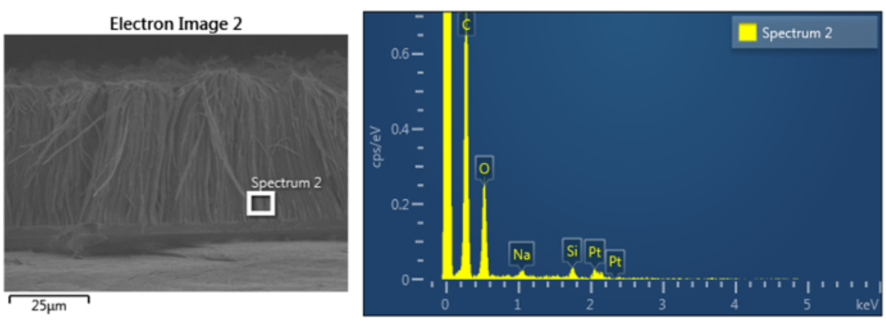

Figure 3: Result of EDX analysis after the etching of nano-micro multiscale structures fabricated using an AAO filter. Please click here to view a larger version of this figure.

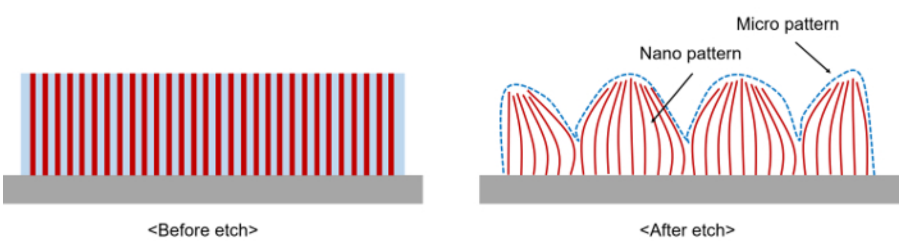

Figure 4: Schematic for the fabrication of a nano-micro multiscale structure by aggregation of nanofibers after complete etching. Please click here to view a larger version of this figure.

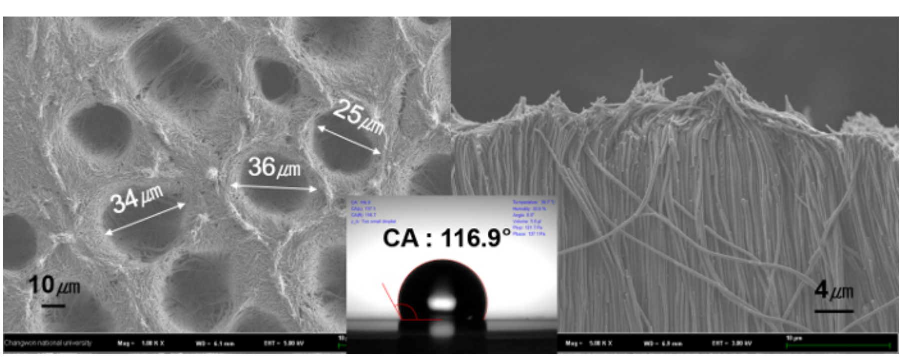

Figure 5: Contact angle after OTS coating on the surface and nano-micro structure. Please click here to view a larger version of this figure.

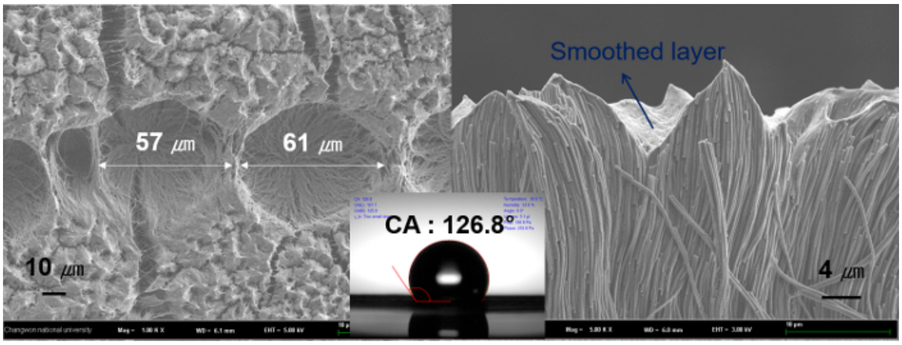

Figure 6: Contact angle after UV ozone treatment on the surface and nano-micro structure. Please click here to view a larger version of this figure.

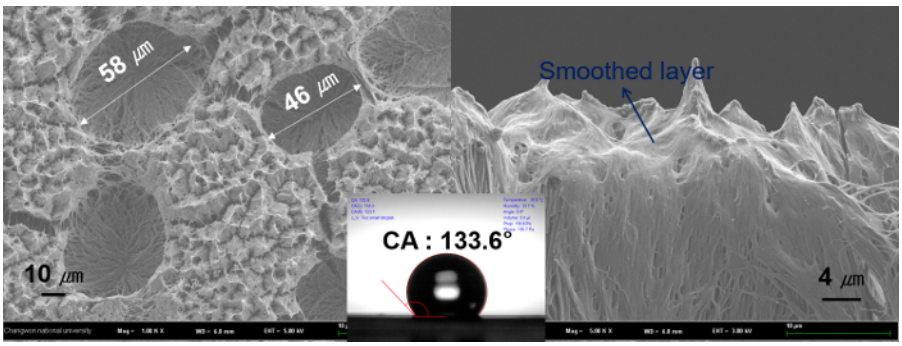

Figure 7: Contact angle after sequentially performing OTS coating and UV ozone treatment on the surface and nano-micro structure. Please click here to view a larger version of this figure.

Discussion

The key step in fabrication of the self-aggregated nanofiber assembly is to ensure that the brittle AAO filter does not break when applying the resin with the rubber rollers. In fact, it should be ensured that the AAO filter does not break at any point before the etching step. Because the AAO filter is 25 mm in diameter, the size of the substrate is approximately 30 x 30 mm.

The self-aggregated nanofiber assembly allows us to provide various functional surfaces through the proper surface treatment. After imprinting, the primary surface is hydrophilic, but it can be modified and become hydrophobic by being subjected to UV ozone treatment and surface energy change after OTS coating. In addition, the proposed multiscale porous structures can be converted to a slippery surface via the liquid lubricant-infusion process.

The surface with nano-micro multiscale structures is opaque, possibly owing to the irregularity of the aggregated nanofibers, and this characteristic can be employed in optical applications. Thus, in subsequent studies, we will investigate the optical characteristics of the substrate using a UV-Vis-IR spectrometer. We expect that the optical properties of such surfaces can be applied to industries that require diffused reflection of light.

Disclosures

The authors have no competing financial interests to disclose.

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