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Repeatable Wettability Conversion between Hydrophobic and Superhydrophilic States on Nonwoven Fabrics Based on Electrospun TiO_2–Poly(dimethylsiloxane) Fibers

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Nonwoven fabrics based on composite fibers of TiO_2 and poly(dimethylsiloxane) (PDMS) are prepared by electrospinning. Nonwoven fabrics based on TiO_2–PDMS fibers are initially hydrophobic and undergo rapid wettability conversion to a superhydrophilic state upon plasma irradiation. Hydrophobicity is rapidly recovered under ambient conditions. This wettability conversion can be repeated by subsequent cycles of plasma irradiation and storage under ambient conditions.

Smart surfaces with a stimuli-responsive change in wettability have received great consideration because of their wide range of potential applications such as microfluidic devices[1] and controllable separation systems.[2] Titanium dioxide (TiO_2) is a candidate to achieve wettability switching because TiO_2 surfaces exhibit wettability conversion from hydrophobic to superhydrophilic states with a contact angle of less than 5° under irradiation with UV light.[3–5] The hydrophobic state of the TiO_2 surface is recovered by storage in the dark for several days or weeks.[6] To achieve further rapid wettability conversion on TiO_2 surfaces, the rate of recovery needs to be increased. Shibata et al. reported that compressive stress accelerates the back reaction of superhydrophilic to hydrophobic states.[7] Recently, we reported TiO_2–PDMS composite films that show wettability conversion between hydrophobicity and superhydrophilicity by alternating irradiation with plasma and storage in the dark.[8] The rate of recovery from superhydrophilic state to hydrophobic one was significantly increased by the presence of PDMS. However, the rate of recovery is still slow and requires further improvement.

In this work, nonwoven fabrics based on TiO_2–PDMS fibers were fabricated, and their wettability conversion upon alternating plasma irradiation and storage in the dark was investigated. The fabrics show rapid wettability conversion between hydrophobic and superhydrophilic states because of the properties of PDMS and the high surface roughness of the nonwoven fabrics with a 3D porous structure.

Nonwoven fabrics based on TiO_2–PDMS fibers were prepared as follows: PDMS (3 g, Aldrich, 432997), titanium tetraisopropoxide (1.5 g, Wako, 207-08176), and tetrahydrofuran (1.5 mL) were mixed and then stirred for 1 h. The solution was loaded into a syringe with a nozzle, which was connected to a positive electrode from a high voltage generator. A grounded metallic plate covered with a piece of aluminum foil and placed 15 cm from the nozzle was used to collect the fibers. The voltage was set at 15 kV. The obtained electrospun fiber was then calcined at 100, 200, 300, 400, or 500 °C (denoted as 100, 200, 300, 400, and 500) for 3 h in air.

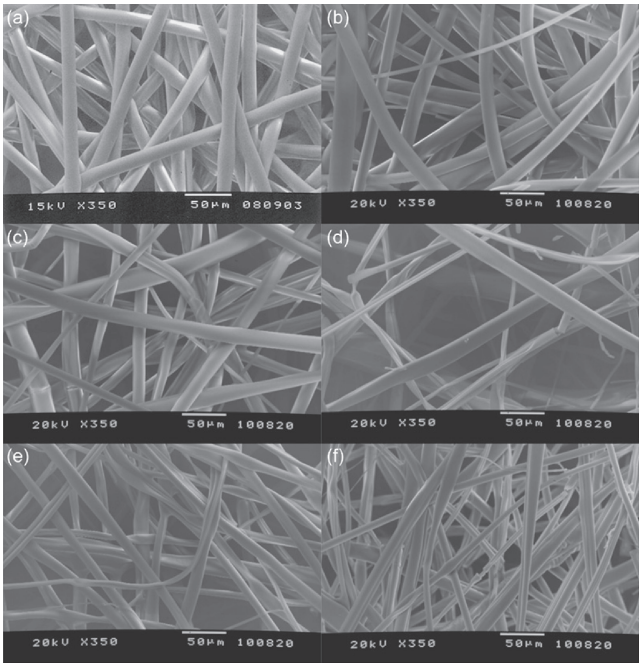

Figure 1. SEM images of TiO_2–PDMS fibers before (a) and after calcination at (b) 100, (c) 200, (d) 300, (e) 400, and (f) 500 °C.

Plasma irradiation was carried out using RF-induced oxygen plasma in a plasma etching system (BP-1, Samco) at a power of 100 W for 5 min and a pressure of 20 Pa.

SEM images of the as-spun and calcined TiO_2–PDMS composite fibers are presented in Figure 1. The fibers had an average diameter of 14.8 µm and a smooth, uniform surface before calcination. After calcination, the average diameter of the fibers decreased to 13.6, 12.6, 9.53, 9.15, and 8.17 for the 100, 200, 300, 400, and 500 samples, respectively, because PDMS can decompose and TiO_2 crystallizes at such temperatures.

Calcination should induce structural changes in PDMS. IR spectra obtained for the TiO_2–PDMS fibers before and after calcination are shown in Figure 2. The peak at 2964 cm^{-1} is attributed to $\nu(CH_3)$ of PDMS. The intensity of the peaks decreased following calcination because of decomposition of PDMS.

Nonwoven fabrics based on TiO_2–PDMS fibers exhibited wettability conversion between hydrophobic and superhydrophilic states upon plasma irradiation. Before calcination, the nonwoven fabrics were hydrophobic with a contact angle of

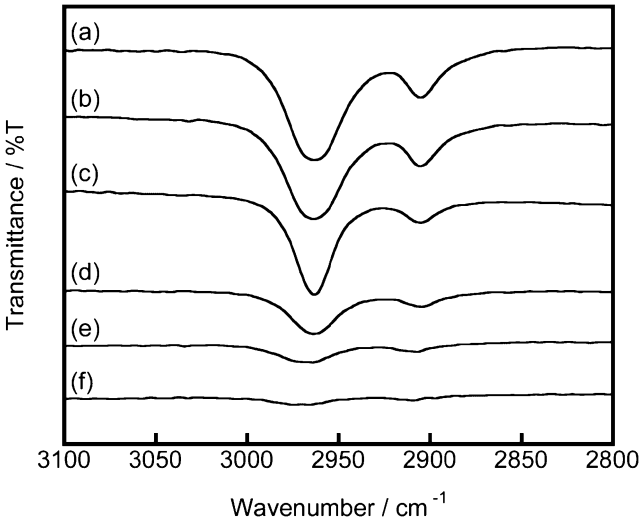

Figure 2. IR spectra of TiO_2–PDMS fibers before (a) and after calcination at (b) 100, (c) 200, (d) 300, (e) 400, and (f) 500 °C.

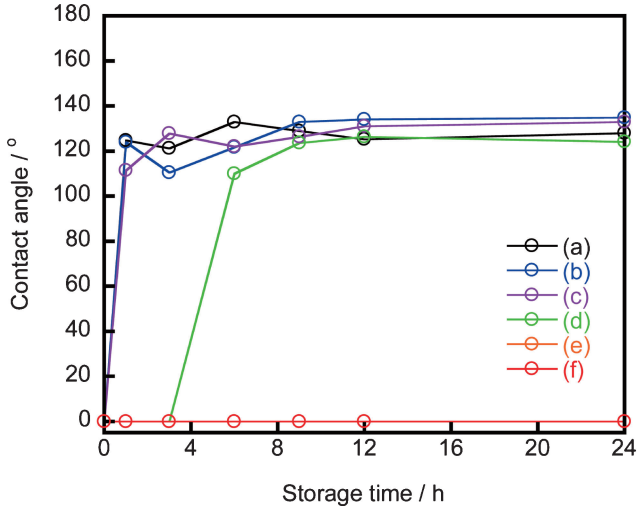

Figure 3. Changes of contact angle as a function of time for TiO_2–PDMS fibers before (a) and after calcination at (b) 100, (c) 200, (d) 300, (e) 400, and (f) 500 °C.

146°. After plasma irradiation for 5 min, the TiO_2–PDMS fibers became superhydrophilic with contact angles of less than 5°, which is due to the release of a methyl group and the formation of a silanol group of PDMS.[8] The contact angles of the nonwoven fabrics gradually increased with time in the ambient air after plasma irradiation, as shown in Figure 3. This is caused by diffusion of low-molecular-weight chains of PDMS from the bulk film surface.[9] This change of contact angle is remarkable for an uncalcined nonwoven fabric. The change in wettability from superhydrophilicity to hydrophobicity for the nonwoven fabrics before calcination takes 1 h. However, the rate of recovery of the contact angle is decreased for the nonwoven fabrics following calcination at higher temperature. For example, recovery takes more than 24 h for the TiO_2–PDMS fibers

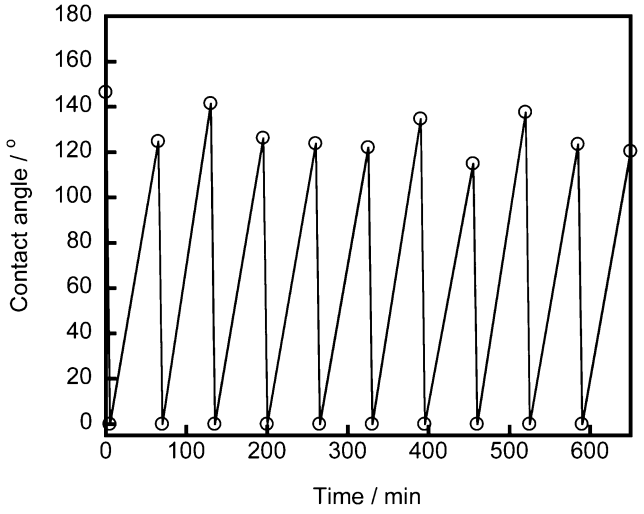

Figure 4. Reversible hydrophobic–superhydrophilic conversion of uncalcined TiO_2–PDMS fibers by alternate plasma irradiation and storage in the dark.

following calcination at 400 or 500 °C, which is caused by the decreased amount of PDMS, as seen in the IR spectra above.

An interesting phenomenon was observed: repeated changes of wettability between hydrophobicity and superhydrophilicity were observed by alternating plasma irradiation and storage in the dark. The contact angles of the uncalcined nonwoven fabrics significantly decreased following irradiation with plasma, but the fabrics rapidly recovered to a hydrophobic state after 1 h at room temperature. This plasma irradiation–storage in the dark cycle was repeated 10 times, as shown in Figure 4.

TiO_2–PDMS films become superhydrophilic after irradiation with plasma but take several days to return to a hydrophobic state.[10–14] In the case of the nonwoven fabrics, it takes just 1 h, which should be because of the high surface roughness originating from the 3D open structure of the nonwoven fabrics. Increased surface roughness enhances the contact angle compared with that for a flat surface.[15–22]

In summary, nonwoven fabrics based on composite fibers of TiO_2 and PDMS were prepared by electrospinning. The diameter of the TiO_2–PDMS fibers could be controlled by varying the temperature used for calcination. The nonwoven fabrics initially display hydrophobicity and undergo rapid wettability conversion to superhydrophilicity upon plasma irradiation. Hydrophobicity is recovered in the dark. Such wettability conversion between hydrophobic and superhydrophilic states is due to of the properties of PDMS and the high surface roughness of the nonwoven fabrics with a 3D porous structure.

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