Nanocharacterization and Nanofabrication of a Nafion Thin Film in Liquids by Atomic Force Microscopy

Kazuo Umemura,*[,†,‡] Tong Wang,[§] Masahiko Hara,[§] Reiko Kuroda,[⊥] On Uchida,[†] and Masayuki Nagai[†]

Research Center for Energy and Environment Science, Musashi Institute of Technology, 1-28-1 Tamazutsumi, Setagaya, Tokyo 158-8557, Japan, Kamoshita Planning, 2-15-1 Shibuya, Shibuya-ku, Tokyo 150-8944, Japan, Frontier Research System, RIKEN, 2-1 Hirosawa, Wako-shi, Saitama 351-0001, Japan, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan, and Kuroda Chiromorphology Project, ERATO-SORST, 4-7-6 Park Building, Komaba, Meguro-ku, Tokyo 153-0041, Japan

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We demonstrated the nanocharacterization and nanofabrication of a Nafion thin film using atomic force microscopy (AFM). AFM images showed that the Nafion molecules form nanoclusters in water, in 5% methanol, and in acetic acid. Young's modulus E of a Nafion film was estimated by sequential force curve measurements in water and in 5% methanol on one sample surface. $E_{water}/E_{5\%\ methanol}$ was 1.75 ± 0.40, so the film was much softer in 5% methanol than in water. Even when solvent was replaced from 5% methanol to water, Young's modulus was not recovered soon. We showed the first example of the mechanical properties of a Nafion film on the nanoscale. Furthermore, we succeeded in fabricating 3D nanostructures on a Nafion surface by AFM nanolithography in liquids. Our results showed the new potential of the AFM nanolithography of a polymer film by softening the molecules in liquids.

1. Introduction

Nafion, a perfluorosulfonate cation-exchange polymer, is one of the most popular compounds used as a solid electrolyte for fuel cells, especially for direct methanol fuel cells (DMFCs).[1−4] For the use of fuel cells, Nafion polymers are attached on an electrode surface as a thin film.

The structure of Nafion films has been intensively studied because it is one of the most important factors in maximizing the energy conversion efficiency of fuel cells. Gebel et al. reported that Nafion polymers expanded in various solvents (e.g., 43% in water and 209% in methanol) because a Nafion molecule has both hydrophobic and hydrophilic parts.[5] The expansion of a Nafion film has been reported by several authors using macroscopic methods.[6,7]

The surface structures of Nafion films have been characterized by atomic force microscopy (AFM) in air.[8−15] For example, James et al. observed clusterlike structures of a Nafion film by tapping-mode AFM. In the report, humidity during the observation was varied from 9 to 34% to study the movement of clusterlike structures (5 to 30 nm) on the Nafion surface.[11] Kanamura et al. observed ion channels on a Nafion surface using a surface potential measurement mode of an AFM.[12] They indicated that the ion channels, which were 40 to 100 nm in diameter, appeared when a droplet of an electrolyte solution was deposited on the Nafion surface in air.

There are a few reports of wet Nafion films studied by AFM. Lehmani et al. dropped an aliquot of water on a dried Nafion film and then observed it in air.[13] Recently, Affoune et al. observed a Nafion film that was stored in water and in methanol prior to AFM observation.[14,15] They found, by AFM observation in air, that a Nafion surface stored in water was much rougher than that stored in methanol. In their experiments using tapping mode AFM, the rms values of a Nafion surface were 34.595 and 4.059 in the case of water and methanol, respectively. They suggested that the difference in roughness originated from the expansion of Nafion molecules in methanol.

Although wet Nafion films were observed in air by several authors, there is no example of AFM imaging in liquids. In general, when a wet sample is imaged in air, a strong adhesion force is induced by water molecules at the interface of the tip and the sample.[16] For this reason, imaging in liquids is an important approach to defining nanostructures of a wet surface precisely. Furthermore, force curve measurement holds potential for studying mechanical properties of a Nafion film although it has never been employed.

However, nanolithography using AFM is one of the most attractive new techniques for producing nanodevices including biochips, nanotransistors, and nanohard disks.[17−20] In particular,

* Corresponding author. E-mail: kumemura@sc.musashi-tech.ac.jp. Tel: +81-3-5707-2100 ext. 2419. Fax: +81-3-5707-1171.

† Musashi Institute of Technology.

‡ Kamoshita Planning.

§ Frontier Research System.

|| The University of Tokyo.

⊥ Kuroda Chiromorphology Project.

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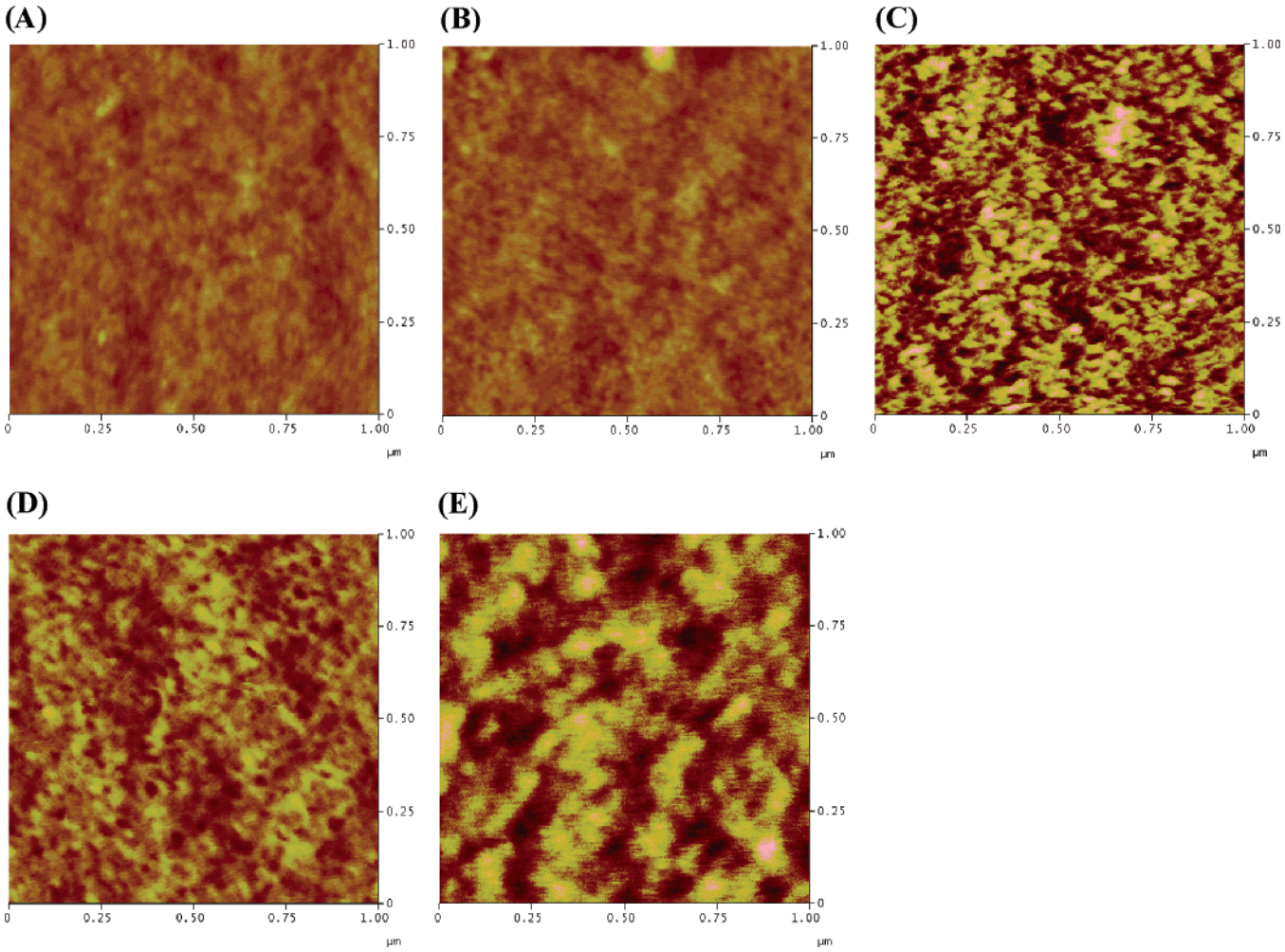

Figure 1. AFM images of Nafion films obtained in tapping mode. Imaging was carried out in air (humidity was 30% in A and 70% in B), in water (C), in 5% methanol (D), and in acetic acid (E). The image size was 1 μm in A−E.

fabricating nanostructures by the mechanical scratching of a sample surface by an AFM probe is one of the most popular methods.[17,18] An AFM probe contacts the sample surface without oscillation in the mode. If a certain area of the sample surface is scanned with higher force than in another area, then the area can be selectively scratched by friction between the tip and the sample surface.

Although AFM nanolithography has great potential in material science, there are several technical difficulties that should be overcome. One serious problem is the regulation of the height and/or depth of the fabricated structures. Although 3D structures can be fabricated on a sample surface, the surface is just peeled in most of the previous reports.[17,18] Even if a sample surface was scratched by a strong force, it does not mean that the height or depth of the structures increased according to the force value. Furthermore, sometimes scratched surfaces were just disordered without fabricating 3D structures, especially in polymer samples.[17]

We demonstrated for the first time the nanocharacterization and nanofabrication of a Nafion film in liquids, not only in air, using AFM in this study. Applying force curve measurements and AFM nanolithography to the study of a Nafion film is a new approach in comparison with that reported in previous papers.

2. Materials and Methods

Nafion 117 (5 w/v in 2-propanol), which was manufactured by DuPont (Wilmington, DE), was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). Fifty microliters of the Nafion solution was dropped onto a metal disk and dried in air. The diameter of the formed Nafion film was around 1 cm.

A commercially available AFM (NanoScopeIIIa, Veeco Inc., Santa Barbara, CA) was used. A silicon (20 to 40 N/m) cantilever was used for tapping mode in air. A silicon nitride (0.1 N/m) cantilever was used for contact mode in air and tapping mode in the liquid. In the case of imaging and measurements made in a liquid, 100 μL of pure water, 5% methanol (95% pure water), or acetic acid (99.9%) was dropped onto a dried Nafion film, and the sample was set in an AFM liquid cell. Force values for imaging and scratching were estimated by force curve measurements.

Imaging in air and in liquid was carried out in tapping mode or contact mode. For fabricating nanopatterns, contact mode was employed with a silicon nitride cantilever (0.1 N/m). The AFM unit was stored in a plastic chamber when the humidity was controlled during measurements.

Force curve measurements in air and in liquids were carried out with a silicon nitride cantilever (0.06 N/m) in contact mode. Prior to injecting solvents into an AFM liquid cell, force curves were captured several times in air in order to define the sensitivity of a cantilever. Then, water or 5% methanol was injected into the AFM liquid cell through a silicon tube. After stabilizing laser values of the AFM unit, force curves were obtained in water and in 5% methanol on one sample. When solvents were replaced between water and 5% methanol, more than 5 mL of solvent was injected into the cell. The

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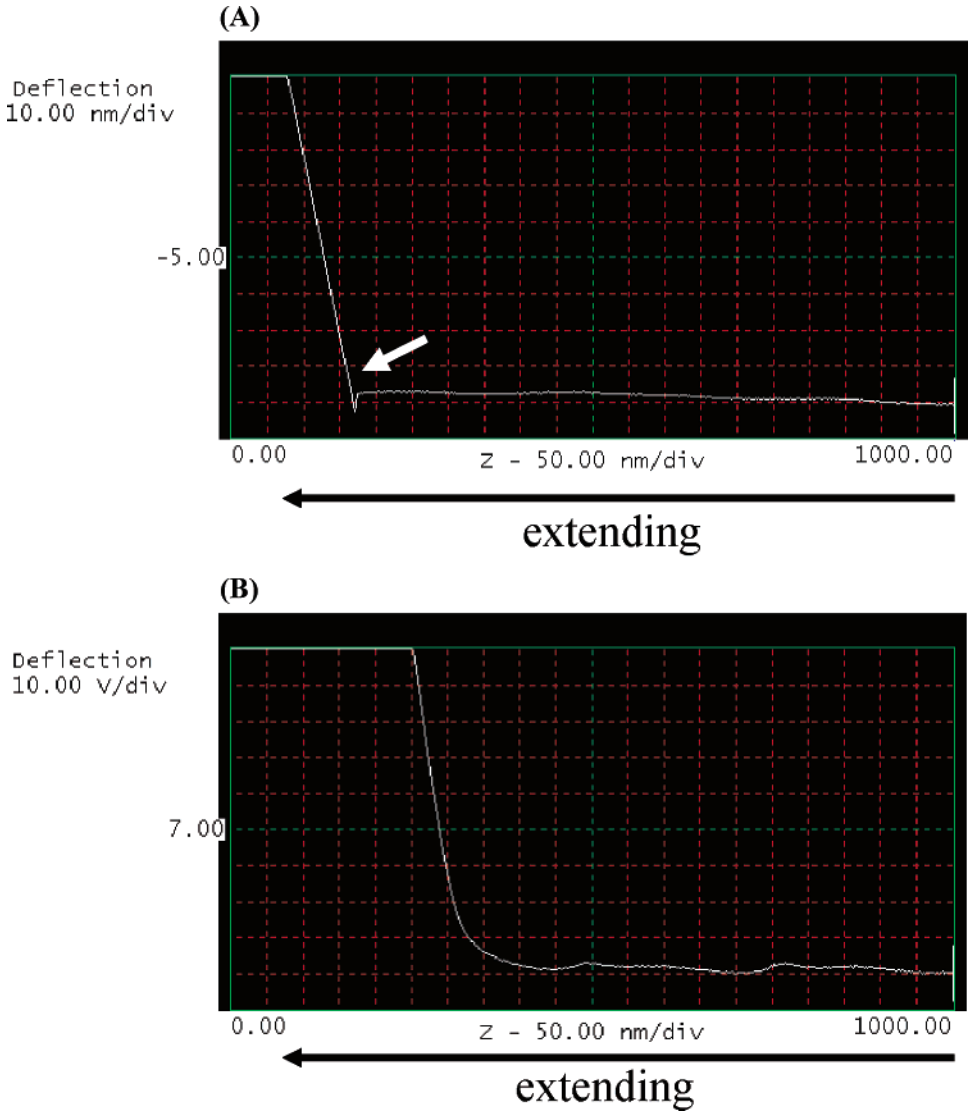

Figure 2. Force curves obtained between a Nafion film and a silicon nitride AFM tip. The measurements were carried out in air (A) and in 5% methanol (B).

volume of the liquid cell and the silicon tube was less than 1 mL, so the solvents should be replaced completely by this procedure.

Young's modulus E was calculated according to the Hertz model with the following equation as described before.[21]

$$z - z_0 = d - d_0 + \sqrt{\frac{k(d - d_0)}{(2/\pi)[E(1 - \nu^2)]\tan(\alpha)}}$$

The Poisson ratio ν was assumed to be 0.5. The half opening angle of the indenting cone of the AFM tip α was 18°, corresponding to the specifications of the manufacturer. The deflection of a cantilever d and the movement of a piezo z were measured from hundreds of force curves.

3. Results and Discussion

3.1. Characterization of a Nafion Surface. Figure 1 shows AFM topographs of a Nafion film observed in air, water, 5% methanol (95% water), and acetic acid. The images clearly show that the Nafion surface is covered with nanoscale clusters under all conditions, although the surface was macroscopically flat and uniform. The size of the clusters observed in water (Figure 1C) was 10 to 20 nm in width although the size in air (Figure 1A and 1B) was much smaller. rms values of clusters on a Nafion surface were around 1.0 and 1.9 nm in air and in water, respectively.

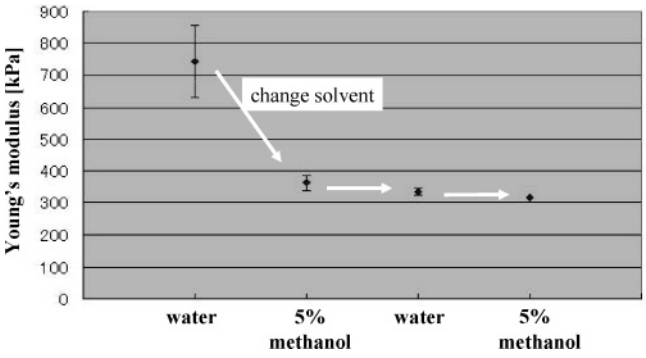

Figure 3. Typical example of the Young's modulus of a Nafion film obtained by sequential force curve measurements in water and in 5% methanol. Solvents were sequentially replaced on one Nafion surface (water, 5% methanol, water, and then 5% methanol). When 5% methanol was injected instead of water, Young's modulus was dramatically decreased.

AFM imaging was also carried out in 5% methanol (95% water) and in acetic acid, respectively. A rather flat surface was

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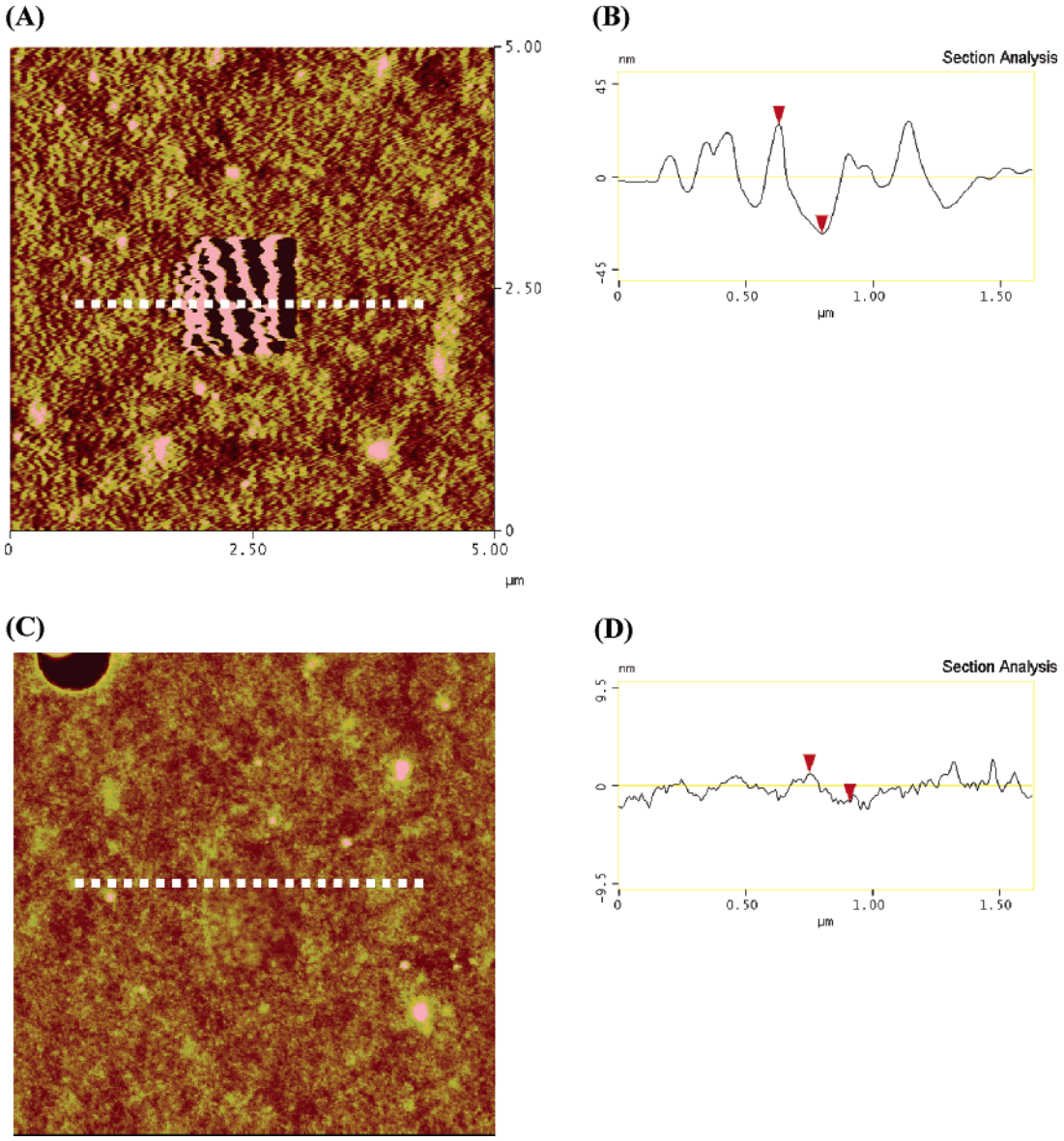

Figure 4. (A and C) AFM images of Nafion surfaces that were modified by AFM nanolithography in air. Contact mode (A and B) and tapping mode (C and D) were employed for the modification. B and D are cross sections of A and C, respectively. White dotted lines in A and C indicate the positions where cross sections were taken. The image size was 5 μm in A and C.

observed in 5% methanol (Figure 1D). However, large clusters of over 100 nm in diameter were observed in acetic acid (Figure 1E). rms values of the surfaces were around 1.7 and 3.0 nm in 5% methanol and acetic acid, respectively.

As described in the Introduction, Affoune et al. stated that the rms value of a Nafion film stored in water was much larger than that stored in pure methanol when they observed the films in air.[16] In our data, the rms value in water (1.9 nm) was not much larger than that in 5% methanol (1.7 nm) when we observed the samples in liquids. There are two possible ideas to explain this difference. First, we prepared a Nafion thin film by ourselves with a Nafion solution. In the previous paper, they purchased an already-prepared Nafion film from the manufacturer. Second, the differences in the environmental condition during the AFM observation may affect the results.

The effect of humidity on nanostructures of a Nafion film was also characterized by imaging in air. Although the humidity was gradually varied from 30 to 70%, no dynamic change in the surface structures due to the humidity variation was observed (Figure 1A and B). It took 1 h to vary the humidity from 30 to 70%. Our data suggests that the hydration of Nafion molecules did not rapidly change the surface structures over the 30−70% range. Our results supplement previous information reported by James et al. that indicated structural changes in Nafion structures in the 9−34% range.[11]

Figure 2 shows typical force curves obtained in air (Figure 2A) and in 5% methanol (Figure 2B). The force curve obtained in air showed a straight line after the AFM tip touched the sample surface (see the arrow in Figure 2A). It suggests that a Nafion film in air behaves like a hard surface under a force of 100 nN. In contrast, the force profile in 5% methanol showed a gradual curve, not a straight line, when the tip pushed the sample surface (Figure 2B). This means that the sample surface yielded under the stress added by the tip. Force curves obtained in water also showed gradual curves.

To verify the softness of Nafion films in liquids, sequential force curve measurements were carried out. Solvents were replaced as follows: (1) from water to 5% methanol, (2) from 5% methanol to water, and finally (3) from water to 5% methanol. In this procedure, force curves were obtained with the same

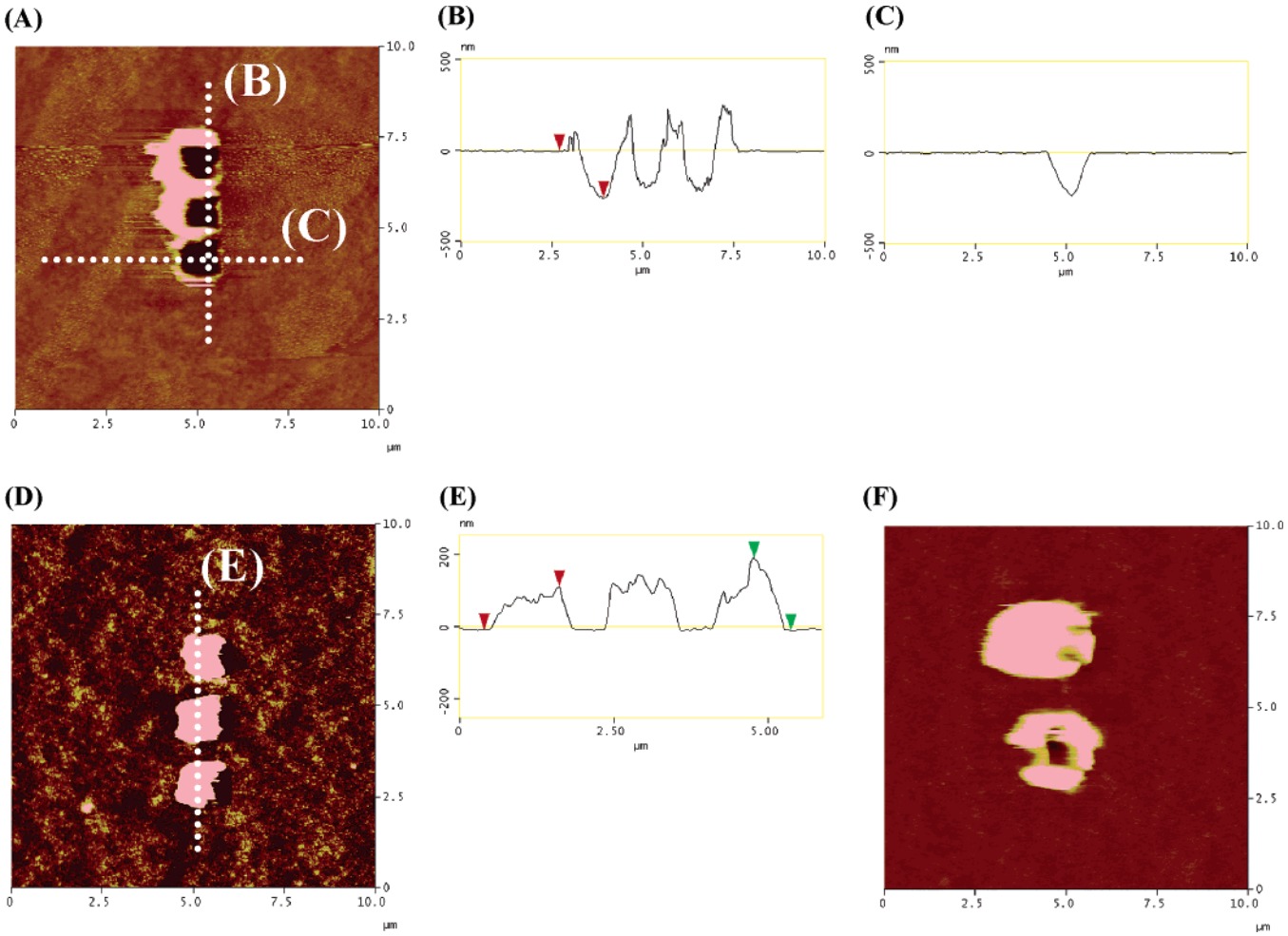

Figure 5. (A, D, and F) AFM images of Nafion surfaces that were scratched by AFM nanolithography in water. B and C are cross sections of A. E is a cross section of D. White dotted lines in A and D indicate the positions of cross sections. The upper object in F was fabricated by scratching in one direction 12 times. The direction of an AFM tip was varied to 0, 90, 180, 270° for every three scratchings in the case of the bottom object in F. The image size was 10 μm in A, D, and F.

Nafion sample and the AFM tip. Figure 3 shows typical results of the sequential measurements in water and in 5% methanol. Young's modulus E of a Nafion surface was estimated using more than 10 typical force curves under each condition.

In water, the estimated Young's modulus was 740 ± 110 kPa after the initial injection. When the solvent was replaced with 5% methanol, the value was changed to 360 ± 20 kPa. Then, even when the solvent was again replaced with water, the value was not increased. Several authors reported that the volume increase in a Nafion film in methanol is larger than that in water (e.g., 43% in water and 209% in methanol).[9−11,15,16] The dramatic change in the Young's modulus in our data probably reflects the volume increase in 5% methanol. Furthermore, our results suggest that adsorbed methanol molecules are not easily released from the Nafion film.

The sequential measurements were repeated with six samples and six cantilevers to examine the reproducibility. The value of the elastic modulus fluctuated from 400 to 750 kPa in water and from 240 to 360 kPa in 5% methanol. The fluctuation might have originated from the variation in the AFM tips or cantilevers. However, the ratio of the estimated Young's modulus in water and in 5% methanol ($E_{water}/E_{5\%methanol}$) was rather stable for each combination of tip and sample. The $E_{water}/E_{5\%methanol}$ value that was estimated with hundreds of force curves in six independent measurements was 1.75 ± 0.40. The data directly showed that a Nafion film was softened in 5% methanol on the nanoscale.

3.2. Fabrication of Nanostructures on a Nafion Surface. The fabrication of nanostructures on a Nafion film was demonstrated in air, in water, and in 5% methanol in contact mode and in tapping mode. We think that the softening of Nafion molecules caused by the hydration in liquids is probably effective in producing 3D nanostructures.

Figure 4 shows AFM images of scratched Nafion surfaces obtained in contact mode (Figure 4A) and in tapping mode (Figure 4B) in air. When contact mode was employed, the central area (one μm square) was scratched five times with 80 nN of vertical force to make a nanostructure; after that, a large area (5 μm^2) was scanned with the lowest force to visualize the scratched area. As a result, the scratched area showed wavelike structures instead of a square hole. The maximum distance between the top and the bottom of the wavelike structure was around 55 ± 16 nm. Even when a stronger force (up to 160 nN) was employed for the scratching, similar results were obtained. It seems that the phenomenon is a typical problem in the AFM nanolithography of polymers.[18]

By the use of tapping mode, clear structural change was not observed although more than 5 nN of tapping force was employed (Figure 4B). The usual force value for imaging is less than 1 nN in tapping mode. An obscure scanning trace was just visualized on a highly contrasted image (arrow in Figure 4B). The data indicate that the tapping mode was not suitable for creating

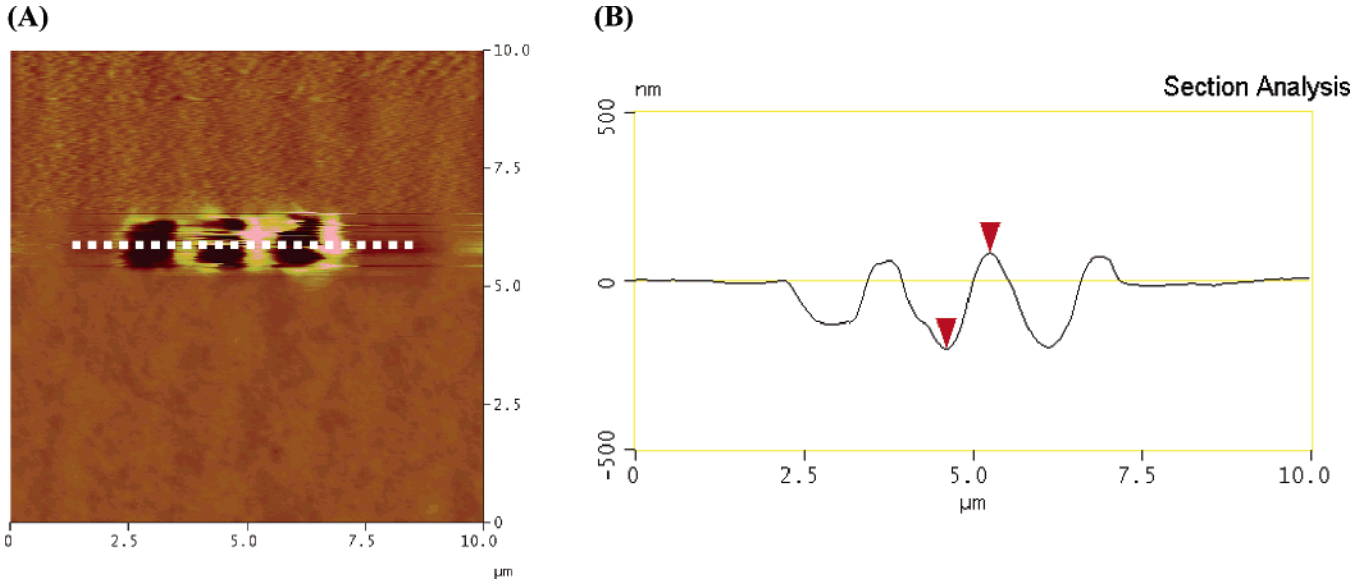

Figure 6. (A) AFM image of a Nafion film that was modified by an AFM tip in 5% methanol. B is a cross section of A. The white dotted line indicates the position of the cross section. The image size was 10 μm in A.

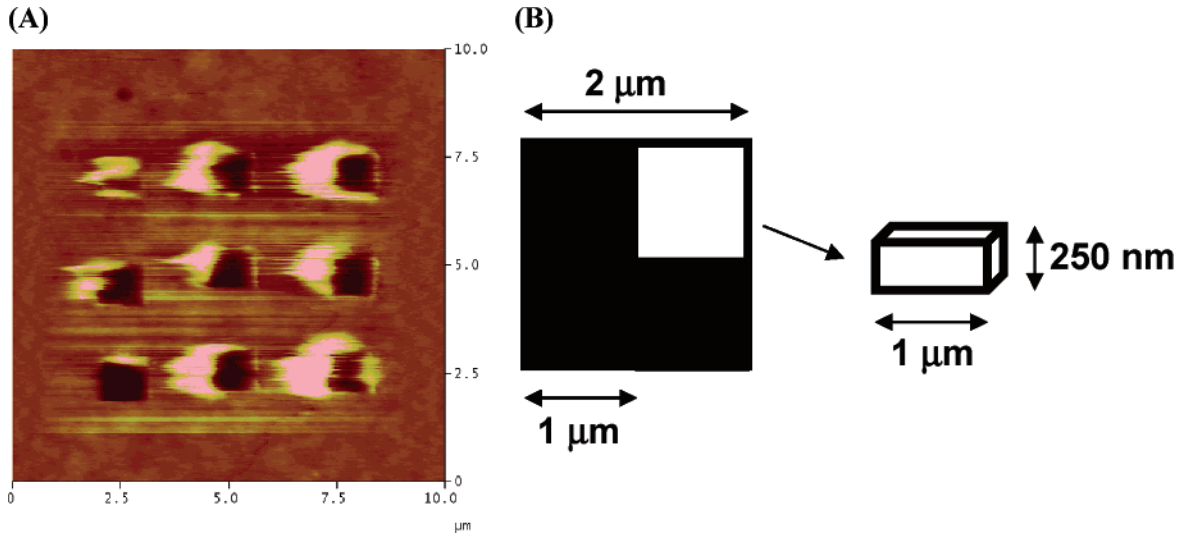

Figure 7. (A) AFM image of a nanopattern fabricated in autoscan mode. (B) Schematic view of a unit of the fabricated patterns. The image size was 10 μm in A.

nanostructures although the force hardly showed any effect on the Nafion surface.

Scratching a Nafion surface in liquids showed completely different results. Figure 5A shows a typical AFM image of a Nafion surface that was scratched in contact mode in water. Three isolated holes were clearly fabricated by varying force values. The force values were 40, 60, and 80 nN for the upper, middle, and bottom holes, respectively. The depth of the fabricated holes was measured to be 230 $\pm$ 36 nm from a cross-sectional measurement (Figure 5B and C). The data clearly indicated that the AFM nanolithography in liquids could produce 3D structures on polymer surface although it was not achieved in air. We think that the softening of polymers by hydration is the key factor in the results.

By using this method, swelled structures of 250 $\pm$ 28 nm in height were sometimes fabricated, although the fabrication mechanism was not clear (Figure 5E). Further experiments are necessary to regulate the shape of the swelled structures; however, we were able to make a unique structure using this phenomenon (Figure 5F). When the tip angle that determines the direction of scratching was sequentially changed by 0, 90, 180, and 270° every three scans, doughnutlike structures were fabricated (bottom object in Figure 5F). The vertical distance from the top to the bottom of the fabricated object is almost 300 nm in the highest region. In contrast, when the surface was scratched in one direction 12 times, then a simple lump was fabricated (upper object in Figure 5F). These data suggest that various 3D nanostructures can be fabricated by this method.

The fabrication of nanostructures could also be carried out in 5% methanol (Figure 6). The conditions of the nanolithography process are exactly the same as those in water. The distance between the top and bottom of a hole was around 240 $\pm$ 36 nm. This result was identical to that obtained in water. Although a Nafion surface in 5% methanol is much flatter than that in water, nanolithography could be carried out smoothly without modifying the scratching condition. However, nanolithography did not work well in acetic acid. We think that an AFM tip was easily contaminated with Nafion molecules in acetic acid.

Figure 7A shows a typical nanopattern obtained via an autoscan command of the AFM. The locus of scratching was programmed on the AFM software so that a certain area was scratched automatically. An area of 1 μm^2 was scratched inside an area of

2 μm^2 in this case (Figure 7B). If we assume that the averaged depth of a hole is 250 nm, then the surface area of the scratched part should be 2 μm^2 including the area of the wall parts. Thus, the surface area was increased 20% (from 4 to 5 μm^2) as a result of nanolithography. The value can be increased if much more detailed nanostructures are fabricated. In general, increasing the surface area with nanopatterns or nanoparticles is effective for improving the function of various devices, thus it is one of the most important approaches in nanotechnology. We believe that the nanofabrication technique will be effective in improving proton conductivity and/or lowering the methanol crossover of fuel cells.

4. Conclusions

Our data clearly revealed the solvent effects on a Nafion surface from the point of view of structures and mechanical properties. In particular, an estimate of elasticity by force measurements showed a new aspect, although structures of Nafion films have been studied by AFM. Additionally, nanofabrication by AFM nanolithography was demonstrated in liquids for the first time. Our data showed that AFM nanolithography in liquids is effective in fabricating 3D structures on a polymer surface, especially on a hydrated polymer surface.

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