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| Description  |  |

# **Super Water-Repellent Treatment of Various Cloths by Deposition of Cat-CVD**

## **PTFE Films**

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**(Revised)**

### **Abstract**

Poly-tetra-fluoro-ethylene (PTFE), “Teflon” in commercial name, films prepared by catalytic chemical vapor deposition (Cat-CVD), often called “Hot-Wire CVD”, are deposited on various cloths of cotton, cotton denim, nylon and polyester. After deposition on such cloths, they show super water-repellent property without impairing breathability. Whole surface of fibers of those cloths is completely covered with PTFE layers which form reticulated sharp convex-concave network structures with a size of a few  $\mu\text{m}$  or less in pitch. The super water-repellent property can be seen even at the back side of the cloths when PTFE films are deposited only at the front side.

**Key Words;** Water repellence, Hydrophobicity, Cat-CVD, PTFE, Cloths, Fibers

## I. INTRODUCTION

Water repellent treatments are widely used for processing cloths. In most cases, cloths are dipped in fluorinated solution or sprayed by such solutions for the treatments. Contrary to this solution process, this paper is to show another approach to add water repellent property on cloths of cotton, cotton denim, nylon, and polyester by depositing water repellent films by a dry process. As the conventional dry method to deposit various high-quality films at low temperatures at which cloths can be used, plasma enhanced chemical vapor deposition (PECVD) method is well-known and widely used particularly in semiconductor industry. However, this method sometimes suffers from the plasma damages on feeble substrates, and also the conformal deposition on complicated structures is not usually easy with PECVD.

In this paper, as a dry process, the catalytic chemical vapor deposition (Cat-CVD) is presented.<sup>1,2</sup> In the method, molecules of source gases are decomposed by catalytic cracking reactions with heated catalyzing metal wires, and thus, high quality films can be obtained at low substrate temperatures near to room temperature (RT) without any damages due to plasma. This is also known as the method to obtain high quality films with conformal coverage on substrates with complicated structures.<sup>3</sup> Since heated metal wires are used, this method is often called Hot Wire CVD<sup>4</sup> or Hot Filament CVD<sup>5</sup>.

Cat-CVD was originally developed in 1980's to prepare inorganic films such as amorphous-silicon (a-Si),<sup>6-8</sup> silicon-nitride (SiN<sub>x</sub>),<sup>9</sup> aluminum-nitride,<sup>10</sup> aluminum-oxide,<sup>11</sup> and silicon dioxide.<sup>12</sup> In 1990's, K. Gleason and her group succeeded in making fluorocarbon films such as poly-tetra-fluoro-ethylene (PTFE) ("Teflon" in commercial) films by this technology, although they called the method as "hot-filament CVD" because of no confirmation of catalytic cracking reaction in this system.<sup>13</sup> Since then, they had succeeded in obtaining various organic films,<sup>14</sup> and in 2000's, they also discovered the way to increase deposition rate enormously and to reduce the temperatures of metal wires by using cracked initiators.<sup>15</sup> They have already showed the water repellent property of cotton after depositing PTFE films by their hot-filament CVD;<sup>16</sup> however, no systematic studies have not been carried out on this water repellent property of cloths, as far as the authors know.

This paper is to show the results of the further systematic studies on the water-repellent property on various cloths after deposition of Cat-CVD PTFE films. It is found that PTFE films prepared by Cat-CVD can cover whole surface of fibers of cotton, cotton denim, nylon, and polyester by forming reticulated sharp convex-concave network structures with a size of a few  $\mu\text{m}$  or less. The super water-repellent property with contact angle (CA) over 150° for a water-droplet can be easily realized for such Cat-CVD PTFE-coated

cloths, keeping breathability of cloths.

## II. FUNDAMENTALS FOR Cat-CVD PTFE DEPOSITION

Cat-CVD apparatus used in the present studies is schematically drawn in Fig. 1. The source gas molecules are decomposed by the catalytic cracking reactions with a heated catalyzing metal wire. As a source gas, hexa-fluoro-propylene oxide (HFPO) gas was used. This HFPO is liquid at RT and in 1 atomic pressure. However, if it is pumped in vacuum, it is easily vaporized and can be used as a source gas. K. Gleason and her group have already discovered that if per-fluoro-octane-sulfonyl fluoride (PFSO) is mixed with HFPO as an initiator, the deposition rate can be increased over 1  $\mu\text{m}/\text{min}$ .<sup>15</sup> However, here, we used only HFPO as a source for obtaining PTFE films.

The temperature of catalyzer,  $T_{\text{cat}}$ , was set at about 800°C to 1,200°C. Thus, the samples on the substrate holder suffer from the thermal radiation from the heated wires. However, the areal density of catalyzing wires was not so high; for instance, 6 wires were set in an area of 15 cm  $\times$  15 cm ( $A \times B$ ) as shown in Fig.1. The distance between the catalyzing wire and the substrate holder,  $D_{\text{cs}}$ , was kept at about 12 cm, and the deposition time was usually shorter than 20 min. Therefore, the heating up due to the thermal radiation from the heated catalyzing wire could be suppressed by keeping the temperature

of substrate holder low enough. The real temperatures of samples placed on a substrate holder which was cooled by cooling water could be kept at RT for several tens min deposition at least. Actually, the organic light emitting diode (OLED) which could not survive in the temperatures over 100°C was successfully covered with Cat-CVD passivation films without any degradation of OLED performance.<sup>17-19</sup>

In Cat-CVD, the selection of catalyzing materials is one of the keys to obtain high-quality films with a certain deposition rate. We have already studied and reported the relationship between the deposition rate and catalyzing material by depositing PTFE films with various catalyzing materials such as nickel-chromium (NiCr), Inconel-600, stainless steel (SUS)-304, iron (Fe), molybdenum (Mo), nickel (Ni), titanium(Ti), tantalum (Ta) and tungsten (W).<sup>20</sup> However, for just confirmation of catalytic cracking reactions in this system, here, we demonstrate the similar experimental results in Fig.2.

Figure 2 shows the infrared (IR) absorption spectra of PTFE films deposited on crystalline silicon wafers by Cat-CVD with various catalyzing materials and various  $T_{cat}$ 's. The PTFE films were prepared with a flow rate of HFPO gas,  $FR(HFPO)$ , at 16 sccm, gas pressure during deposition,  $P_g$ , at  $1.5 \times 10^{-3}$  Pa and the substrate temperature,  $T_s$ , at water cooling (W.C.) temperature, say, about RT. The IR absorption peaks assigned as C-F<sub>2</sub> bonding vibrations are seen in the figure. This confirms that the film is PTFE. The

deposition time is fixed at 30 min for all samples in the figure, and thus, the difference of IR absorption peak height simply corresponds to the difference of film thickness. The film with larger IR peaks corresponds simply to thicker film prepared with high deposition rates. From the figure, we can know what material is suitable for high rate deposition of PTFE films.

It is apparent that the deposition rate is largest when NiCr is used as catalyzer. Inconel-600 and SUS-304, which both contain Ni atoms in alloys, show relatively high deposition rates. However, the deposition rates prepared with pure metals such as even Ni catalyzer are not so fast. For instance, the deposition rate with Ni catalyzer was about 1/5 of that with NiCr catalyzer. When W was used as a catalyzer, which was often used for a-Si or SiN<sub>x</sub> deposition, the deposition rate was almost 1/10 of the case with NiCr catalyzer. This is probably due to the reason why two types of sites are required on the surface of catalyzer for dissociative adsorption of a HFPO molecule. That is, the results exhibit that the decomposition is not simply carried out by the thermal process but by the catalytic cracking process

Although the deposition rate was largest when NiCr was used, here, we used W of 800°C as a catalyzer to obtain PTFE films. The deposition rate was still 20 nm/min and it was easy to adjust the film thickness. The deposition parameters used in the present

experiments are summarized in Table I.

### **III. WATER REPELLENT PROPERTY OF PTFE FILMS ON GLASSES AND VARIOUS CLOTHS.**

Here, we show the actual water repellent property of PTFE films deposited on glasses or cloths of cotton, cotton denim, nylon, and polyester by Cat-CVD. As glass substrates, we used Corning 1737 glasses. In the present study, we used a W wire with a diameter of 0.5 mm as a catalyzer and kept  $T_{\text{cat}}$  at 800°C, the flow rate of HFPO gas, FR(HFPO), at 8 sccm and  $T_s$  at RT as summarized in Table I.

Figure 3 shows the photographs of a water droplet on 50 nm-thick PTFE films which were prepared on glass and various cloths such as cotton, cotton denim, nylon, and polyester, with  $P_g$  of  $3 \times 10^{-3}$  Pa and  $T_s$  at RT. The values of CA evaluated from the photographs are also indicated in Fig 3. Super water-repellency is defined as CA exceeding over 150°. The results almost show the super repellency in case of PTFE deposition on cloths.

Figure 4 shows the photograph of a water droplet on cotton denim after the treatment of water repellency by the conventional solution process. CA is 136.9° and smaller than that on Cat-CVD PTFE films. CA values on cotton cloth may have ambiguities due to its

fluctuation of surface state. However, since the fluctuation of CA appears smaller than  $\pm 5^\circ$ , the difference between CA shown in Fig. 4 and that in Fig. 3 demonstrates the difference of deposition method of water repellent films. That is, by the present dry process, more water repellency can be expected than the case using the conventional solution process.

#### **IV. MECHANISM OF WATER REPELLENCY OF CAT-CVD PTFE FILMS**

Here, the relationship between the thickness of PTFE films and water repellency is studied for the PTFE films deposited on glasses and cloth of cotton denim. Figure 5 shows the photographs of a water droplet on various thick PTFE films on glasses and Fig. 6 shows similar photographs on cloths of cotton denim. PTFE films were prepared with  $P_g=3 \times 10^{-3}$  Pa and  $T_s=RT$ .

The hydrophilicity can be seen from a water droplet on glass substrate without coating PTFE films as shown in Fig.5; however, after deposition of 50 nm-thick PTFE, the glass sample immediately shows water repellency as already shown in Fig.3. The water repellency is increased with increasing PTFE thickness as indicated CA values in Fig. 5, and super water repellency can be seen for the thicknesses over 200 nm.

Similar tendency is seen for PTFE films on cloths of cotton denim as shown in Fig. 6.

When the thickness of PTFE films exceeds 200 nm, CA exceeds over 150° and the samples show super water repellency for both glass substrates and cloths of cotton denim.

We have observed the surface morphology of PTFE films by using atomic force microscope (AFM), to know the mechanism of appearance of super water repellency.<sup>21</sup> The AFM images of PTFE surfaces deposited on glass substrates are shown in Fig. 7 with the values of CA. Although these AFM images have been already reported in Ref.21, just for convenience of explanation, we show the images again here. The PTFE film shown in Fig. 7(a) is prepared by Cat-CVD with  $P_g=2.25 \times 10^{-3}$  Pa and that shown in Fig. 7(b) is prepared with  $P_g=3.75 \times 10^{-3}$  Pa.

In Fig. 7, the root mean square (RMS) of surface roughness is also indicated. When CA increases from 133° to 158°, the surface roughness is likely to increase. RMS increases from about 20.5 nm to 38 nm for this increase of CA. In addition, the pitch of surface roughness appears to decrease to the order of a few  $\mu\text{m}$  or less; that is, roughness becomes sharper when CA increases. It is well known that the water repellency depends on the surface structures, and that CA becomes large when the surface has sharp convex-concave structures. From the AFM images, we can conclude that the water repellency observed in PTFE films originates from the structures on the surface of Cat-CVD PTFE films, although the effect using fluorinated films may also exist on water repellency.

Next, we study on the surface structures of PTFE films formed on various fibers of cloths. Figure 8 shows the results of observation by using the scanning electron microscope (SEM) when 200 nm-thick PTFE films are deposited on a cloth of cotton with  $P_g=3.75 \times 10^{-3}$  Pa. In Fig. 8(a), an image of a cotton fiber covered with PTFE film is demonstrated. The PTFE film covers the whole surface of fibers. This means that the coverage by Cat-CVD films is excellent, which appears to cover entirely the surface of fiber. This is also confirmed from the fact that the water repellency can be seen even at the back side of cotton cloth when PTFE films are deposited only on the front side of the cloth.

Figure 8(b) shows the same SEM image observed with larger magnification. Reticulated sharp convex-concave network structures are clearly shown at the surface of PTFE films. The size of a reticulated structure appears to be a few  $\mu\text{m}$  or less. The value is almost equivalent to the pitch of convex-concave structures evaluated from the AFM images. These so small structures may cause the super water repellency, as already indicated from the AFM images.

There has been a report on the surface morphology of Cat-CVD PTFE films, and in the report, the similar morphology was seen in PTFE on crystalline silicon.<sup>22</sup> However, this is the first clear view of the surface morphology of PTFE on fibers with water

repellency.

Similar structure was also made by T. Itoh et al. when they made carbon films on Ni substrates by Cat-CVD using methane ( $\text{CH}_4$ ) as a source gas. Since such carbon films have unique structures with sharp reticulated convex-concave network, they described the films as carbon nanowall.<sup>23</sup> They applied the carbon films to electron field emission. In their case, they used W catalyzer of  $T_{\text{cat}}=1,950^\circ\text{C}$ , which was much higher than the case of PTFE deposition. However, similar sharp standing convex-concave structures may tell us some features of carbon-related films made by Cat-CVD.

Figure 9 shows the similar SEM images of the cotton fibers which were treated for water repellency by using the conventional solution method. Figure 9(a) shows the image of whole fiber and (b) shows the image of magnification of it. Compared with Cat-CVD process, the surface structure cannot be clearly observed. In this case, the property of covered films may directly decide the water repellency. The mechanism of water repellency is apparently different from the conventional wet process.

Since Cat-CVD PTFE films have very complicated reticulated structure, and since the structure appears weak for mechanical stress, one may worry about the lifetime of water repellent property. However, we confirm that super water repellency on cloths of cotton can still remain even for 5 years after PTFE film deposition.

Finally, a photograph of many water droplets on a cotton handkerchief which is covered with 200 nm-thick Cat-CVD PTFE film is shown in Fig. 10. Big water droplets are made on cotton handkerchief for its super water repellency.

## **V. CONCLUSIONS**

Above results can be summarized as follows;

- 1) By deposition of Cat-CVD PTFE films with a thickness of only 50 nm, water repellency can be added onto cloths of cotton, cotton denim, nylon, and polyester.
- 2) By deposition of 200 nm-thick PTFE films by Cat-CVD, super water repellency can be added onto cloths of cotton, cotton denim, nylon, and polyester.
- 3) PTFE films prepared by Cat-CVD completely cover the whole surface of fibers of cloths, and thus, water repellency can be found even at the back side of cloths when PTFE films are deposited only on the front side of cloths.
- 4) Super water repellency originates from the surface structure of a PTFE film. It has reticulated sharp convex-concave network structure with a size of a few  $\mu\text{m}$  or less in pitch.

## **ACKNOWLEDGEMENT**

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## REFERENCES

1. H. Matsumura, [Thin Solid Films](#) **395**, 1 (2001).
2. R.E.I Schropp, [Thin Solid Films](#) **595**, 272 (2015).
3. Q. Wang, S. Ward, L. Gedvias, and B. Keyes, [Appl. Phys. Lett.](#) **84**, 338 (2004).
4. A.H. Mahan, J.Carapella, B.P. Nelson, R.S. Crandall, and I. Balberg, [J. Appl. Phys.](#) **69**, 6728 (1991).
5. S. Matsumoto, T. Sato, M. Kamo and N. Setaka, [Jpn. J. Appl. Phys.](#) **21**, L183 (1982).
6. H. Wiesmann, A.K. Ghosh, T. McMahon, and M. Strongin, [J. Appl. Phys.](#) **50**, 3752 (1979).
7. H. Matsumura, H. Ihara and H. Tachibana, *Proc. of the 18th IEEE Photovoltaic Specialist Conference*, Las Vegas, Nevada, USA, Oct. 21-25, (1985), p.1277.
8. H. Matsumura, [Jpn. J. Appl. Phys.](#) **25**, L949 (1986).
9. H. Matsumura, [J. Appl. Phys.](#) **66**, 3612 (1989).
10. J.L. Dupuie, and E. Gulari, [J. Vac. Sci. Technol. A](#), **10**, 18 (1992).
11. Y. Ogita, S. Iehara, and T. Tomita, [Thin Solid Films](#) **430**, 161 (2003).
12. K. Saito, Y. Uchiyama, and K. Abe, [Thin Solid Films](#) **430**, 287 (2003).
13. S.J. Limb, C.B. Labelle and K.K. Gleason, D.J. Edell and E.F. Gleason, [Appl. Phys. Lett.](#) **68**, 2812 (1996).
14. R. Sreenivasan and K.K. Gleason, [Chemical Vapor Deposition](#) **15**, 77 (2009).

15. H.G.P. Lewis, J.A. Caulfield, and K.K. Gleason, [Langmuir](#) **17**, 7652 (2001).
16. H.G.P. Lewis, J.A. Caulfield, K.K.S. Lau, and K. Gleason, *Technical Digest of Abstract of 2nd Int. Conf. on Hot-Wire CVD (Cat-CVD)*, Denver, USA, (2002), p.351.
17. Y. Ogawa, K. Ohdaira, T. Oyaidu, and H. Matsumura, [Thin Solid Films](#) **516**, 611 (2008).
18. A. Heya, T. Minamikawa, T. Niki, S. Minami, A. Masuda, H. Umemoto, N. Matsuo, and H. Matsumura, [Thin Solid Films](#) **516**, 553 (2008).
19. D. Spee, K. van der Werf, J. Rath, and R. Schropp, [Physica Status Solidi, RRL \(Rapid Research Letters\)](#) **1** (2012).
20. H. Yasuoka, M. Yoshida, K. Sugita, K. Ohdaira, H. Murata, and H. Matsumura, [Thin Solid Films](#) **516**, 687 (2008).
21. M. Takachi, H. Yasuoka, K. Ohdaira, T. Shimoda, and H. Matsumura, [Thin Solid Films](#) **517**, 3622 (2009).
22. K.K.S.A. Lau, H.G. Pryce Lewis, S.J. Limb, M.C. Kwan, and K.K. Gleason, [Thin Solid Films](#) **395**, 288 (2001).
23. T. Itoh, S. Shimabukuro, S. Kawamura, and S. Nonomura, [Thin Solid Films](#) **501**, 314 (2006).

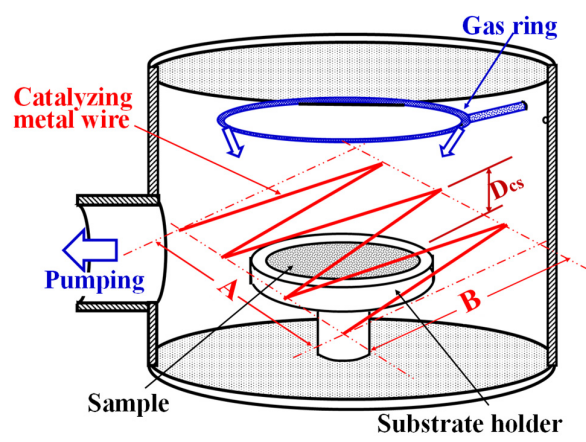
## FIGURE CAPTIONS

- FIG.1 Schematic view of Cat-CVD apparatus used in experiments.
- FIG.2 Infrared absorption spectra of PTFE films prepared by Cat CVD with various catalyzing materials and catalyzer temperatures,  $T_{\text{cat}}$ .
- FIG.3 Photographs of a water droplet on 50 nm-thick PTFE films deposited on glass and various cloths. CA is indicated for each photograph.
- FIG.4 A photograph of a water droplet on a cloth of cotton denim after treatment of water repellency by the conventional solution process.
- FIG.5 Photographs of a water droplet on various thick PTFE films on glasses.
- FIG.6 Photographs of a water droplet on various thick PTFE films on cloths of cotton denim.
- FIG.7 AFM images of surface of PTFE films on glass substrates with (a) PTFE film with  $CA=133^\circ$ , and (b) that of  $CA=158^\circ$ .
- FIG.8 (a) SEM image of PTFE films covering a cotton fiber, and (b) same image with larger magnification.
- FIG.9 (a) SEM image of cotton fiber after the conventional water repellent treatment by solution, and (b) same image with larger magnification.
- FIG.10 A photograph of big water droplets formed by accumulation of many small droplets on Cat-CVD PTFE-coated handkerchief.

TABLE I. Deposition parameters of PTFE films by Cat-CVD.

| Various parameters                                 | Setting conditions  |
|--|---|
| Materials of catalyzing wire                       | NiCr, Inconel 600, Fe, SUS304, Mo,<br>Ni, Ti, Ta, W (Mainly; W) |
| Temperature of catalyzer、 $T_{cat}$                | 800 — 1,200 °C  |
| Spanning area of catalyzer                         | 15 cm×15 cm = 225 cm <sup>2</sup>                               |
| Number of catalyzing wires in above spanning area  | 6   |
| Surface area of catalyzer、 $S_{cat}$               | 14.3 cm <sup>2</sup>  |
| Distance between catalyzer and substrate、 $D_{cs}$ | 12 cm   |
| Temperature of substrate holder、 $T_s$             | Room Temperature = RT   |
| Flow rate of HFPO gas, FR(HFPO)                    | 8 and 16 sccm   |
| Gas pressure during deposition、 $P_g$              | $3.75 - 4.00 \times 10^{-3}$ Pa                                 |
| Types of substrates                                | Glass, Clothes of cotton, cotton<br>denim, nylon and polyester. |

**Figure 1**



**Figure 2**

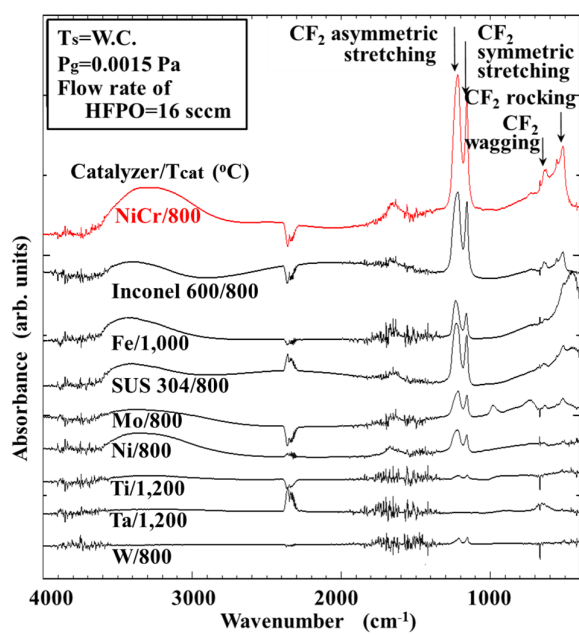


Figure 3

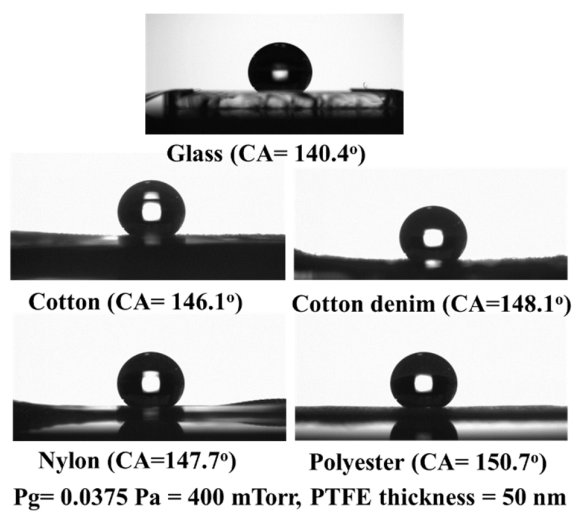


Figure 4

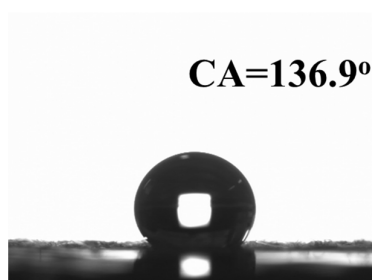


Figure 5

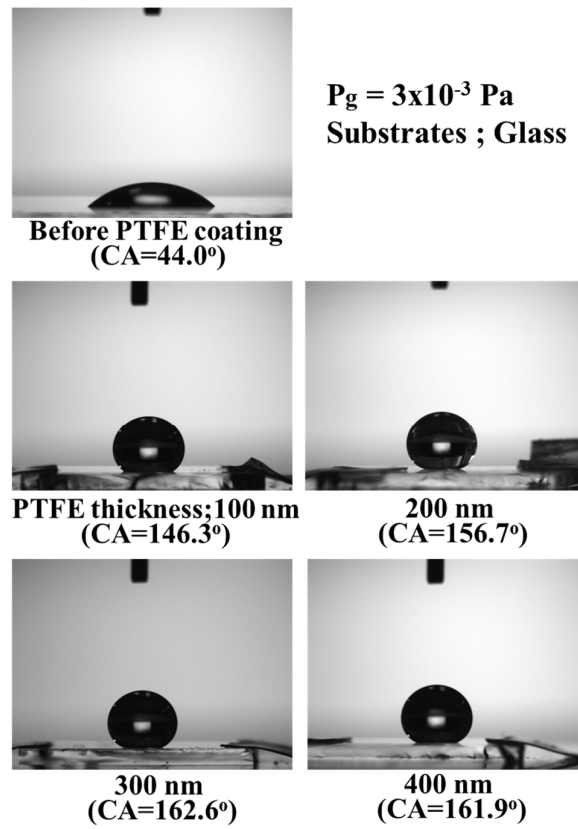


Figure 6

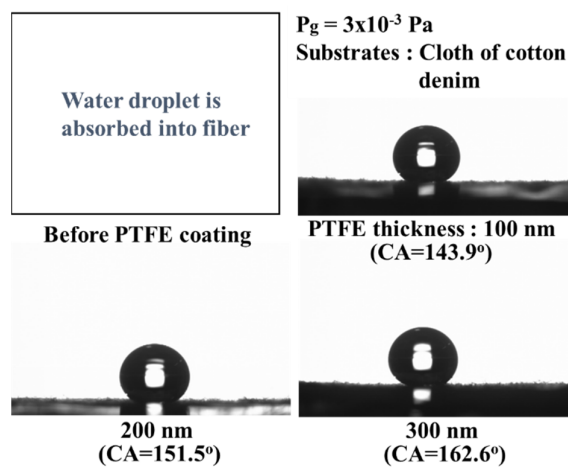
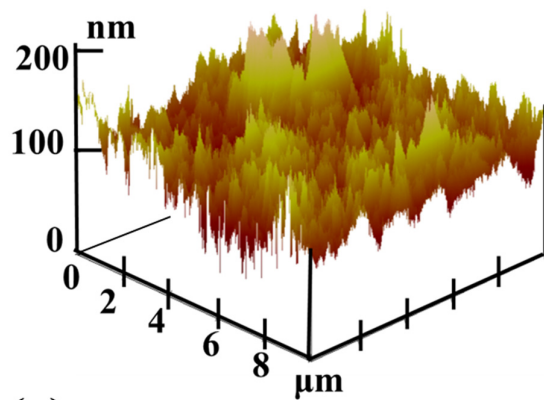
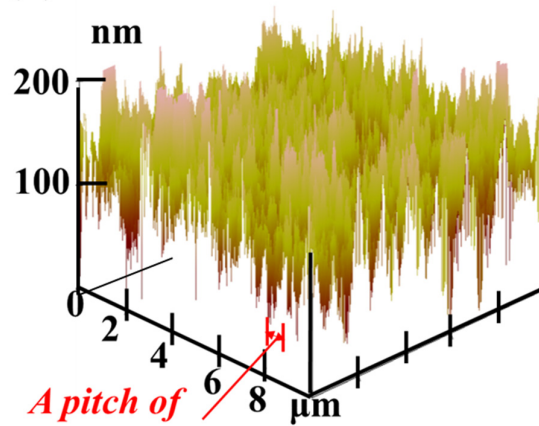


Figure 7

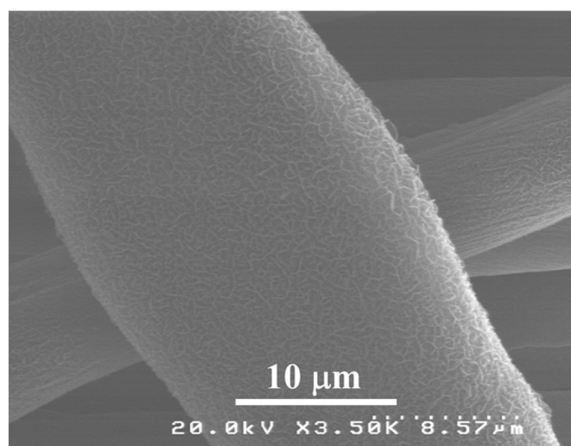


**(a)** CA=133°, RMS=20.5 nm

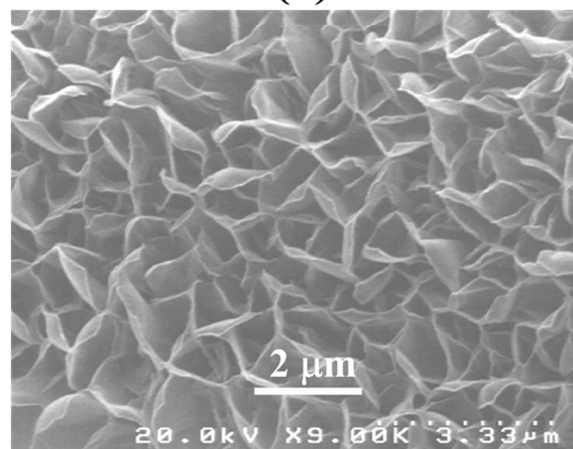


**(b)** CA=158°, RMS=38 nm

Figure 8

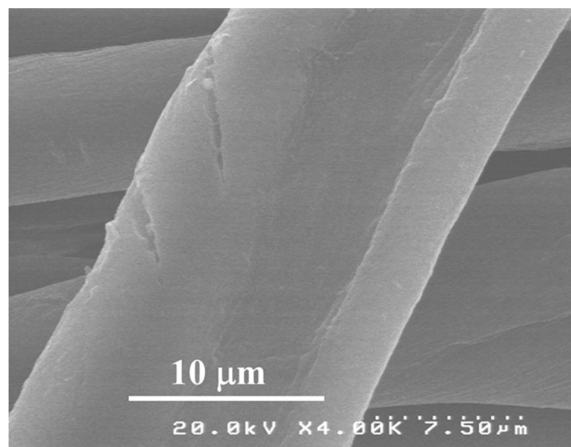


(a)

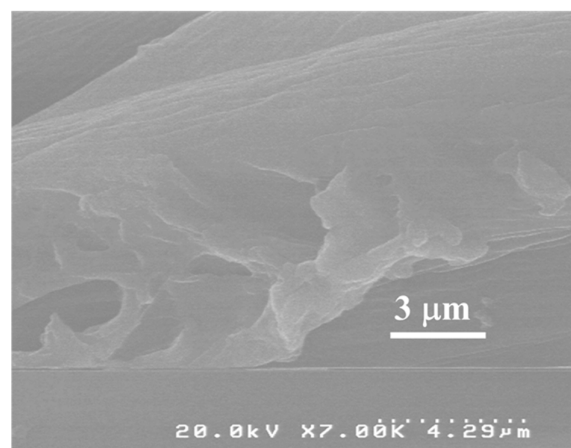


(b)

Figure 9



(a)



(b)

Figure 10

