

# Conversion of Functional Group on PTFE Surface by Argon Plasma Pre-treatment and Polydopamine Coating

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**Abstract.** The mussel-inspired polydopamine (PDA) coating, which is unstable and fragile on poly(tetrafluoroethylene) (PTFE) surface, is now successfully stabilized by using argon plasma treatment as a pre-treatment before conducting PDA coating. In this study, the parameters of plasma including plasma energies, gas pressures and treating time were adjusted to construct a stable PDA coating layer on PTFE surface. Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy were used to characterize the surfaces. The sonication stability of PDA coating layer on plasma treated PTFE surface was evaluated. The robust PDA coating layer reported in this study can act as a reactive platform for further modification and reaction on PTFE.

## 1. Introduction

The Polymer materials are widely used in the field of energy, environment and biomedicines. As one of the common polymeric materials, polytetrafluoroethylene (PTFE) has been used as, for instance, various industrial accessories, water purification membrane and cardiac sheet thanks to its excellent mechanical properties, high flexibility and chemical stability. However, with the development of technology and industry, our demands on materials become more and more strict. The pristine properties of PTFE may not be satisfactory. For example, as biomaterials for artificial heart valves [1] and vessels [2], PTFE still induced the inflammation and infection [3, 4] when it was being implanted into human bodies. To achieve a better application, modification of PTFE is often needed. Unfortunately, the PTFE is hard to be modified because the chemical inertness of its C-F bond. It is hard for common coating methods to make differences when facing the anti-fouling nature of the PTFE.

Polydopamine (PDA) coating, this bio-inspired coating methods has drawn lots of research attention because of its convenient coating process and strong chemical and physical coating stability on almost all kind of material [5]. Dopamine can convert to polydopamine by self-polymerization under atmosphere. However, its coating stability on PTFE has not been well-studied yet.

Our target is to construct a robust PDA coating layer on PTFE surface. This coating layer, which has large amounts of reactive functional groups, can play as a reactive platform for further modification of PTFE. In present study, some new PDA coating methods for PTFE, which applied argon plasma treatment as a pre-treatment, is reported. The parameters of plasma treatment were optimized to achieve sonication-stable PDA coating layer on PTFE surface. Fourier-transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) were used to characterize the surfaces and evaluate the sonication stability of PDA coating layer on PTFE surface. As a result, plasma pretreatment with certain parameters can significantly improve the stability of PDA coating on PTFE surface. This post-modification strategy will expand the application of the PTFE and give more possibility to PTFE.



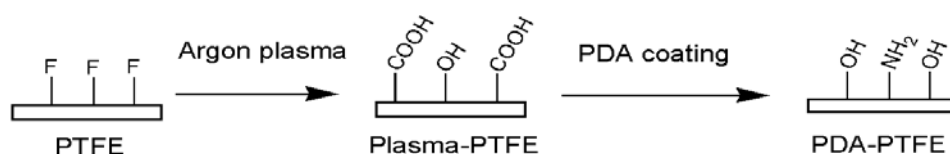


**Figure 1.** The process of plasma treatment and following PDA coating

## 2. Materials and methods

### 2.1. Materials

Tris(hydroxymethyl)aminomethane and 3-hydroxytyramine hydrochloride (Dopamine) was purchased from Tokyo Chemical Industry CO., Ltd.(Tokyo, Japan). Hydrochloric acid was purchased from Kanto Chemical Co., INC (Tokyo, Japan).PTFE substrate was purchased from Sanplatec Co. Ltd. (Osaka, Japan).

### 2.2. Plasma treatment on PTFE

Pristine PTFE substrates were washed by acetone in an ultra-sonic cleaner (US-2R; ASONE CO., Ltd. Osaka, Japan) for 15 min. Then, a plasma reactor (PR500; Yamato Scientific Co. Ltd., Tokyo, Japan) was used to treat PTFE surface by argon plasma with various parameters listed below. After treated by argon plasma, the PTFE surfaces were exposed to atmosphere for 20-min to facile the surface oxidation.

**Table 1.** Conditions of argon plasma treatment used in this research

|     | Plasma energies (W) | Gas pressure (Pa) | Time (Sec) |
|-----|---------------------|-------------------|------------|
| I   | 10                  | 20                | 5          |
| II  | 20                  | 20                | 5          |
| III | 30                  | 20                | 5          |
| IV  | 40                  | 20                | 5          |
| V   | 100                 | 20                | 60         |

### 2.3. PDA coating on plasma treated PTFE

PTFE substrates with or without argon plasma treatments (1.0 cm × 1.0 cm × 0.5 cm) were dipped into a just-made 2 g/L dopamine aqueous solution of pH 8.5 [5]. The reactions were carried out on a shaking table for 24 h under room temperature. The substrates were then thoroughly washed by ethanol and water and dried in a desiccator. The samples were either used for the stability evaluation of the PDA coating or further surface modification.

### 2.4. Stability evaluation of PDA coating on PTFE surface

The PDA coating on untreated PTFE or argon plasma-treated PTFE (Plasma-PTFE) surfaces were subjected to sonication in ultra-sonic cleaner with ethanol to examine the stability on the PTFE surface. The sonication time was ranged from 5 to 90 min. The wastages of PDA coating on surface were determined by characterization of surface. The morphologies of sonicated surfaces were observed by naked eye.

### 2.5. Surface characterization methods

ATR-FTIR (FT-IR/ATR; IMV-4000, JASCO, Tokyo, Japan) was used to characterize the functional groups on PTFE surface. The wastage of PDA coating after sonication was semi-quantified by the average peek ratio of PDA-related function group to PTFE-related functional groups. Five points were

taken by ATR probe. The FT-IR spectra were examined in 64 scans over the range of 650-4000  $\text{cm}^{-1}$  at a resolution of 8.0  $\text{cm}^{-1}$ .

The elemental composition of surfaces was determined by XPS (AXIS-His; Shimazu/Kratos Co. Ltd., Kyoto, Japan) with  $\text{MgK}\alpha$  (15 kV) radiation source at the anode. The releasing angle of photoelectron was  $90^\circ$  from the surface of samples.  $\text{C}_{1s}$ ,  $\text{N}_{1s}$ ,  $\text{O}_{1s}$ ,  $\text{F}_{1s}$  were characterized. All the spectrums were referred to  $\text{C}_{1s}$  peak at 284.7 eV for the binding energy.

### 3. Results and discussions

#### 3.1. PDA coating on argon plasma treated PTFE surface

Figure 2 shows the ATR-FTIR spectra of PDA coated PTFE surface prepared by condition **V** as shown in table 1 and original PTFE surface. PTFE had a simple FT-IR spectrum with two peaks at 1200 and 1150  $\text{cm}^{-1}$ , which correspond to the vibration of  $-\text{CF}_2$  symmetric stretching [6, 7]. A broad band at around 3300  $\text{cm}^{-1}$  was observed, which is assigned to the stretching vibration of N-H and O-H. The broad peaks at 1596  $\text{cm}^{-1}$  and 1510  $\text{cm}^{-1}$  are assigned to ringing C=C and ringing C=N, respectively [8]. After PDA coating, the  $\text{F}_{1s}$  signal disappeared and  $\text{N}_{1s}$  signal appeared in Figure 3, which indicate that PTFE surfaces were covered by PDA. The thickness of PDA coating layers was above 10 nm which estimated from the detection range of XPS.

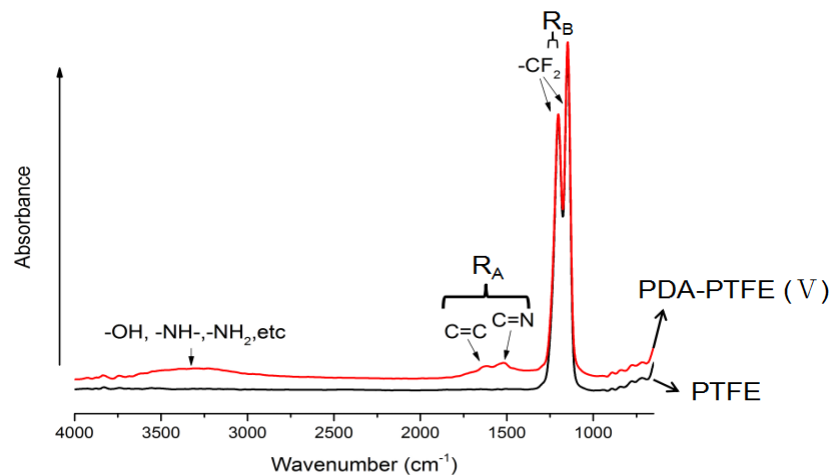


**Figure 2.** The ATR-FTIR spectra of PTFE and PDA-PTFE

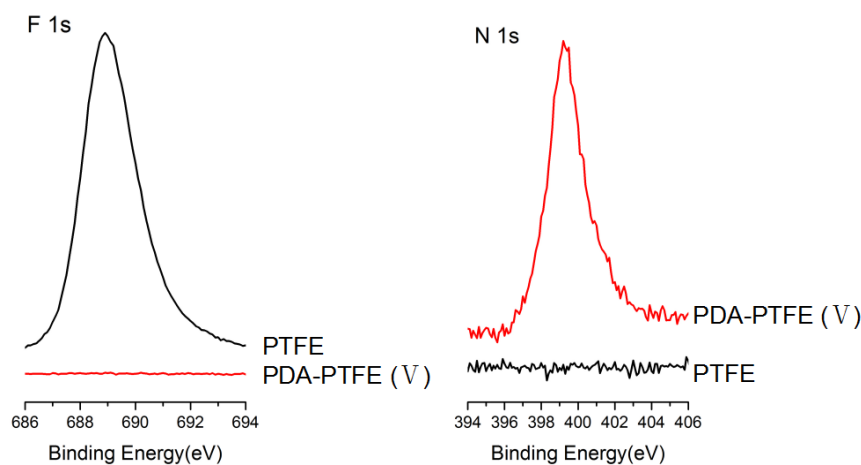


**Figure 3.** The  $\text{F}_{1s}$  and  $\text{N}_{1s}$  XPS charts of PTFE and PDA-PTFE

### 3.2. Sonication stability of PDA coating layer

The sonication stability of the PDA layer on the PTFE surfaces with different plasma treatment parameters in ethanol was quantitatively evaluated using ATR-FTIR measurement. At the first, the peak areas taken by  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  in Figure 1 were defined as Region A ( $R_A$ ) and the peak area taken by  $\nu(-\text{CF}_2)$  at around  $1200\text{ cm}^{-1}$  was defined as Region B ( $R_B$ ).  $R_A$  stands for the amount of PDA-related functional groups on coated surface. The ratio of Region A to Region B ( $R_{A/B}$ ) was used to semi-quantify the wastage of coating layer on the surface during sonication. Figure 4 shows the relationship between sonication time and the  $R_{A/B}$  values on PTFE surfaces. As shown in Figure 4, the coating layers on the PTFE surfaces without plasma pretreatments were eliminated by sonication in five minutes. On the other hand, with the increase of argon plasma energies, the final  $R_{A/B}$  value after 90-min-sonication increased. In other words, more and more PDA moieties remained on PTFE surface. When argon plasma energies are higher than 40 W, the PTFE surfaces could be still well-covered by PDA coating.

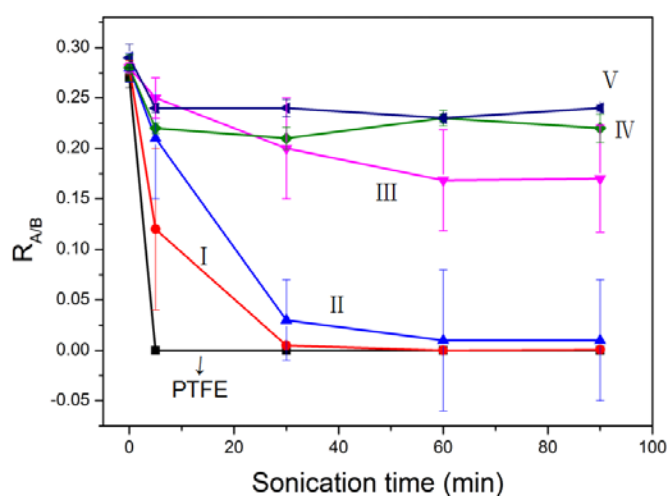


**Figure 4.** Stability evaluation of PDA layer prepared on the PTFE surface and Plasma-PTFE surfaces in various conditions as shown in table 1

The  $F_{1s}$  XPS charts of different samples sonicated for 90 min were collected in Figure 5. The  $F_{1s}$  signal recovered on sonicated surface, which was not pretreated by plasma.  $F_{1s}$  signal on plasma treated (The plasma energies were higher than 40 W) surfaces were still insignificant. The recovery of  $F_{1s}$  signal indicates the significant loss of PDA coating layer on PTFE surface. No obvious recovery was observed when plasma energy was higher than 40 W.

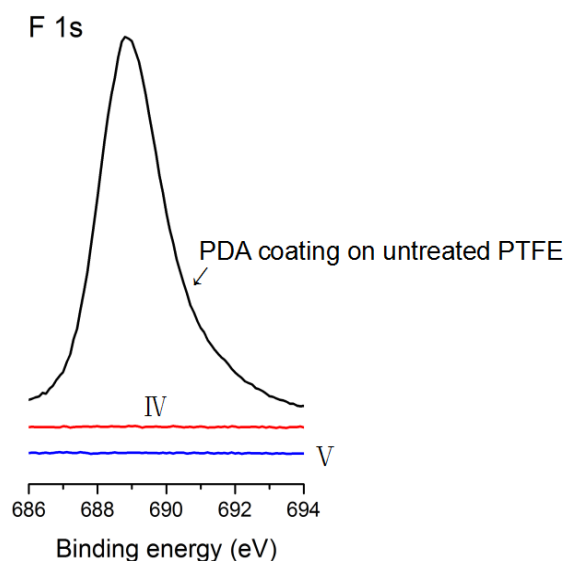


**Figure 5.** Effects of plasma treatment on PTFE before PDA coating process on stability of PDA coating

The results were also supported by Figure 6, which is a photo image of the morphologies of sonicated PDA coated surfaces. Because the PDA coating had a dark-brown color, their morphologies could be easily observed by naked eye.

Above mentioned results indicate that argon plasma pretreatment could enhance the sonication stability of PDA coating layer on PTFE surface. One lower limit of argon plasma parameters to stabilize PDA coating on PTFE surface was found.



**Figure 6.** The morphologies of sonicated PDA coated PTFE. All the samples were sonicated for 90 min

It is considered that argon plasma treatment brought amounts of oxygen-contained functional groups to PTFE surface by generating radicals on the PTFE surface during sputtering and inducing the oxidation of PTFE surface when surfaces contacted with oxygen. These functional groups, such as  $-OH$ ,  $-COOH$  and peroxide, could better interact with the PDA coating layer and lead to a tougher interaction between material surface and coating layer. The plasma energies were related to the amount of functional groups introduced. When argon plasma energies are higher than 40 W, the amount of functional groups were enough to maintain a well-covering PDA coating layer on PTFE.

Also, the wettability on the surface of PTFE may become better after argon plasma treatment. It is one of the possible reasons for the tough interaction achieved by plasma reinforced PDA coating process. However, the mechanism of plasma reinforced PDA coating process has not been understood. Further researches on its mechanism are now being carried out in our research group.

#### 4. Conclusion

As a pretreatment method, argon plasma was used to reinforce the interaction between polydopamine coating layer and PTFE surface. The results indicated that argon plasma treatment with certain parameters could significantly improve the stability of PDA layer. This so-called plasma reinforced PDA coating process could construct a robust reactive platform on chemically inert PTFE surface. The well-covered coating layer, which had massive reactive functional groups such as  $-OH$  and  $-NH_2$ , is available to trigger further modification of PTFE. This coating process will expand the application of PTFE in the fields of energy, environmental and medical industries.

#### 5. References

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