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ABSTRACT

This paper investigated the chemical bonding features and conductivity characteristics of atmospheric pressure plasma (APP) conducting polymerized polypyrrole (pPPy) by iodine (I_2) doping method in coupling and remote conditions, respectively. The I_2 doped APP pPPy film surfaces were analyzed by field-emission scanning electron microscopy (FE-SEM). Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) analyses were used to determine the crystallinity and chemical bond of I_2 doped APP pPPy film for both coupling and remote conditions, respectively. In terms of crystallinity and bonding structure, I_2 doped APP pPPy film, which was obtained by coupling condition, had own advantages, such as existence of abundant multiple bond ($C\equiv C$/$C\equiv N$) with π-electron, improved crystallinity, and lower initial resistance compared to that of remote condition. Whereas, the dense and thick I_2 doped APP pPPy film obtained by remote condition was less hydrated and shown lower resistivity change-rate under ambient air compared to that of coupling condition. Therefore, different resistivity and humidity characteristics of I_2 doped APP pPPy films depending on growth condition such as remote and coupling conditions contribute to increasing the possibility of using the I_2 doped APP pPPy film as flexible electrode-materials.

1. Introduction

Since the conducting polymer (polyacetylene) showing a possibility of metal-insulator transition as a function of dopant concentration was reported for the first time, [1] the conducting polymers have attracted a great deal of attention due to their technological advances with high conductivity and flexibility in broadening the scope of applications, such as polymer light emitting diode (P-LED), flexible electrode-materials, *etc* [2, 3]. Among various conducting polymer synthesis methods, recently, atmospheric pressure plasma (APP) polymerization technique is newly emerging due to its own advantages, such as low cost, low temperature, and "dry process" features [4–9].

However, the conductivity features of these conventional polymers doped by halogen dopants are significantly affected by the ambient humidity. The deficiency of stability in APP polymerized samples' conductivity may be due to the unstable nature of the charge transfer complex with the dopant, for example, iodine (I_2), thereby resulting in a greater ease of diffusion of the I_2 from the film [10]. Most previous our studies have focused on I_2 doping process of APP polymerized polymers in remote condition [11–13]. However, analyses and comparison on initial resistivity and resistivity change-rate features of I_2 doped APP polymerized films have not yet been systemically studied relative to exposure time under ambient humidity especially in coupling and remote conditions, respectively. Note that the coupling condition means the direct contact between the plasma and the substrate, whereas the remote condition means the remoteness of the substrate from the intense and broadened (*i.e.*, glow-like) plasma.

Therefore, in this study, we examined resistivity and resistivity change-rate features of I_2 doped APP polymerized polypyrrole (pPPy) films under ambient humidity in coupling and remote conditions, respectively. Noticeably, the APP polymerization process employed in this study is exactly the same described in our previous work, except for adopting additional I_2 doping process [14]. Accordingly, the morphology and cross-sectional images of I_2 doped APP pPPy were characterized using the field emission scanning electron microscopy (FE-SEM, Hitachi SU8220). The Fourier transform infrared spectroscopy (FT-IR, Frontier) and X-ray photoelectron spectroscopy (XPS, Qwentera SXM) were used to determine the chemical changes induced by the plasma and I_2 doping process. The X-ray diffraction (XRD, MP-XRD DS109) was used to estimate the dependence of the film crystallinity and check the surface morphology. Furthermore, the variations in resistance were also examined to check the suitability of the conductive layer for future display technologies.

2. Experiment set-up

Figure 1 shows a schematic diagram of the experimental setup of the advanced atmospheric pressure plasma jets (APPJs) for (a) APP polymerization and (b) halogen doping processes, respectively. The three jet tubes, arranged in a triangle shape, were wrapped with copper tape as a powered electrode, 10 mm from the end of the jets, which produced a more compact design as each jet was in physical contact with the adjacent jets. Each jet tube was 13 cm in length, with an inner diameter of 1.5 mm and an outer diameter of 3 mm. In addition, glass GT system was adopted to induce further vigorous secondary flow and static pressure of discharge gases. The GT system consists of glass guide-tube and bluff-body. The guide tube was 60 mm in length, with an inner diameter of 20 mm, whereas the bluff-body had an outer diameter of 15 mm. A sinusoidal power source was connected to the powered electrode via a driving circuit with a peak value of 18 kV.

High purity argon (Ar) gas (99.999%) was used as a discharge gas for plasma generation, and its flow rate was 2000 standard cubic centimeters per minute (sccm). The liquid pyrrole monomer (Sigma-Aldrich Co.) was vaporized using a glass bubbler that was supplied by Ar gas at a flow rate of 200 sccm. The sample glass substrates and interdigitated electrodes were mounted on the bluff-body for APP polymerization. The
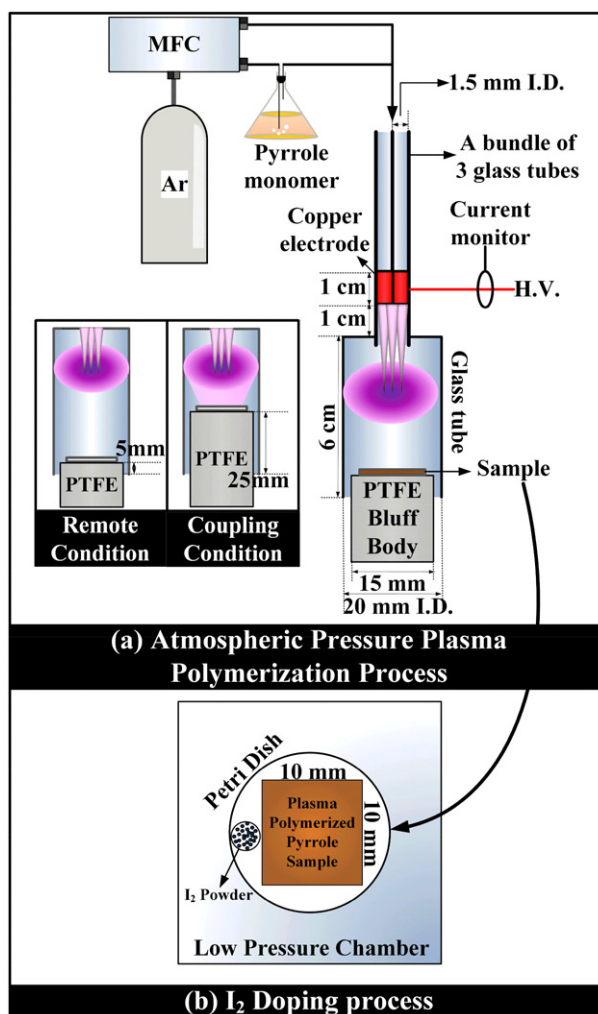
Figure 1. Schematic diagram of the experimental set-up for (a) APP polymerization and (b) halogen doping processes, respectively.

APP polymerization and deposition were conducted for 30 min., and then the APP pPPy films were doped by placing samples in a sealed container containing solid iodine (3 g) for 30 min.

3. Results and discussion

FT-IR and XPS measurements were adopted to check the chemical bonds of atmospheric APP pPPy films introduced by I_2 doping process. Figure 2 shows the FT-IR spectra of I_2 doped pPPy films after APP polymerization on glass substrates relative to coupling and remote conditions, respectively. The FT-IR spectra of these I_2 doped pPPy films were measured between 650 and 4000 cm^{-1}. For both coupling and remote conditions, the broad peaks located at 3285 cm^{-1} corresponding to N-H stretching with hydrogen bonded, aliphatic C-H bonds at 2960 cm^{-1}, multiple bond of C≡C/C≡N peak
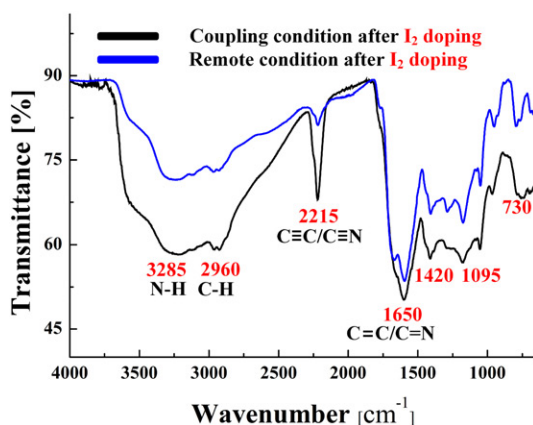
Figure 2. FT-IR spectra of I_2 doped pPPy films on glass substrates after plasma polymerization for 20 min. relative to coupling and remote conditions, respectively.

at $2215\,\mathrm{cm}^{-1}$, and double bond of $C=C/C=N$ peaks at $1650\,\mathrm{cm}^{-1}$, were clearly observed [15, 16]. It is notable that the $C\equiv C/C\equiv N$ triple bond dramatically increased, in the case of coupling condition, indicating the reduction of hydrogen atoms in pPPy films via I_2 doping process, when compared to that of remote condition. The increase of multiple-bonds implies the existence of abundant π-electrons, which affects the conductivity features of APP pPPy films by I_2 doping process. It is also important to note that these significant increases of triple bonds were observed only in the case of coupling condition after I_2 doping process, compared to all cases with and without I_2 doping processes, including our previous work [14]. Whereas, in the case of remote condition, multiple-bonds, such as $C\equiv C/C\equiv N$ triple bond and $C=C/C=N$ double bond with π-electrons, were not significantly changed after I_2 doping process, compared to our previous work [14]. These results imply that the I_2 doping process differently affects the bonding characteristics of APP pPPy films under coupling and remote conditions, respectively.

Figure 3 and Table 1 show the bar-plots presenting of atomic concentration ratio about XPS survey spectra and the percentage of elements identified from the XPS spectrum of I_2 doped pPPy films after APP polymerization on glass substrates relative to coupling and remote conditions, respectively. As shown in Table 1, for coupling condition, the carbon and nitrogen contents increased from 71.1 to 73.0% and from 16.0 to 16.6%, respectively. Whereas, the oxygen contents decreased from 12.1 to 9.3% compared to those of remote condition. The increase of carbon and nitrogen contents well coincided with an increase in the multiple bonds of $C\equiv C/C\equiv N$, as shown in FT-IR analysis, which would be an evidence of better conductivity features in the case of coupling condition. As a consequence, these results indicated that the I_2 doping process had an significant influenced on the bond characteristics of APP pPPy films, especially in the case of coupling condition with direct contact between energetic plasma and sample substrate.

Figure 4 shows the XRD patterns of I_2 doped pPPy films after APP polymerization on glass substrates for 20 min. relative to coupling and remote conditions, respectively. The XRD patterns showed a broad scattering peak from $2\theta = 20 - 25°$. This peak is

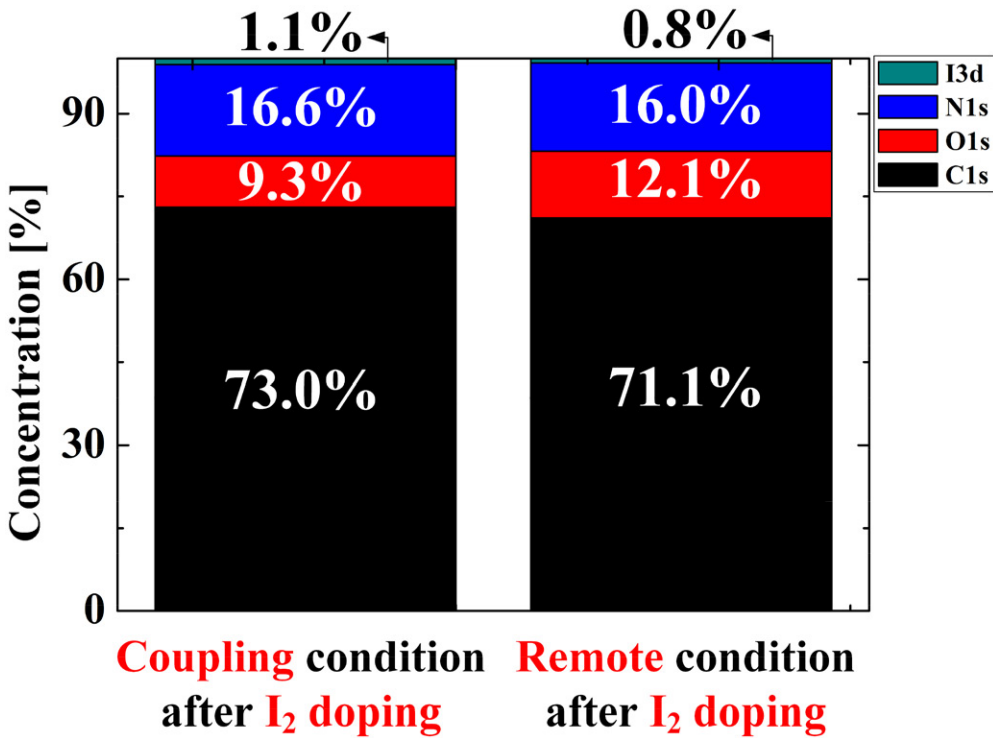**Figure 3.** Bar-plots presenting of atomic concentration ratio about XPS spectra of I_2 doped pPPy films on glass substrates after plasma polymerization for 20 min. relative to coupling and remote conditions, respectively.

Table 1. Atomic percentage by XPS spectra about I_2 doped plasma polymerized pyrrole film prepared on glass substrates for 20 min. under coupling and remote conditions, respectively.

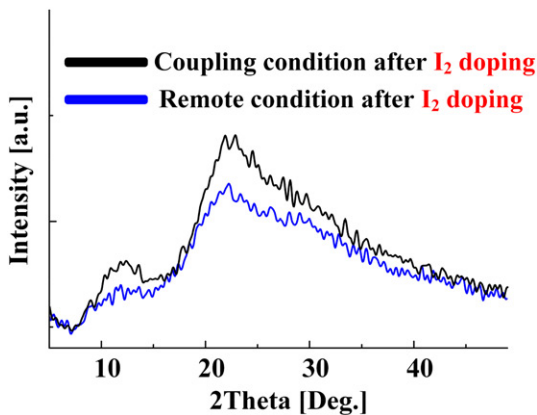| Composition, %	C1s	O1s	N1s	I3d
Coupling condition	73.0	9.3	16.6	1.1
Remote condition	71.1	12.1	16.0	0.8

Figure 4. XRD patterns of I_2 doped pPPy films on glass substrates after plasma polymerization for 20 min. relative to coupling and remote conditions, respectively.
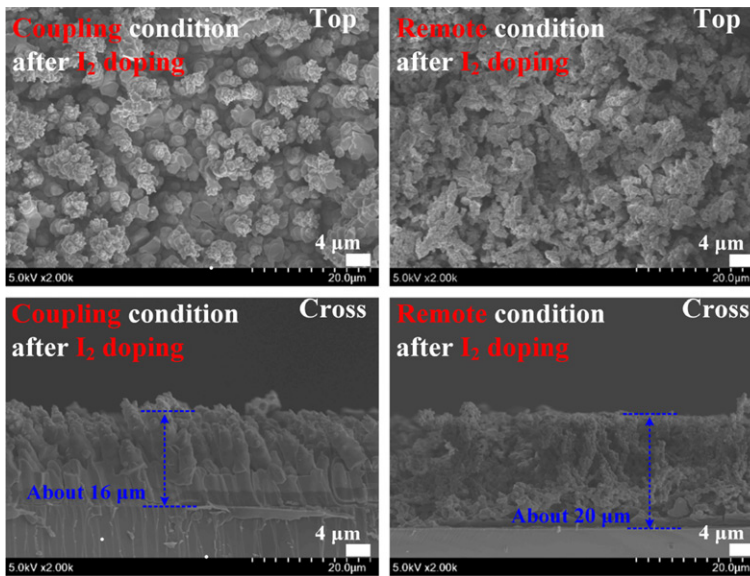
Figure 5. SEM images of I_2 doped pPPy films on glass substrates after plasma polymerization for 20 min. relative to coupling and remote conditions, respectively.

similar to those reported for pPPy by various polymerization methods illustrating plasma polymerized pPPy films [17, 18]. In addition, in terms of crystallinity characteristics, the structural arrangement of APP pPPy films was slightly improved after I_2 doping process in coupling condition. These results indicated that the monomers could be fully cracked in the recombination region during plasma polymerization, enough to satisfy the necessary condition for plasma polymerization in terms of crystallinity. [11]

Figure 5 shows the FE-SEM images of I_2 doped pPPy films after APP polymerization on glass substrates for 20 min. relative to coupling and remote conditions, respectively. In case of coupling condition, after I_2 doping process, the particles were aggregated due to the hydration and I_2 particles. These results are similar to the tendency of the APP polymerized polyaniline nanoparticles vanished and aggregated after I_2 ex-situ doping [13]. Whereas, in case of remote condition, the smaller sizes of pPPy particles were densely obtained and formed as a thick film through I_2 doping process. As shown in the cross-sectional view images, the thicknesses of I_2 doped APP pPPy films were 20 and 16 μm under remote and coupling conditions, respectively. In addition, any remarkable aggregated or vanished APP pPPy features were not observed under the remote condition. These results would be an evidence that the obtained dense and thick APP polymerized films were less influenced by humidity under ambient air after I_2 doping process.

Figure 6 shows the changes in the resistance of pPPy films of I_2 doped pPPy films after APP polymerization on interdigitated electrodes relative to exposure time under ambient air. In case of coupling condition, the initial resistance (R_o) value of I_2 doped pPPy films was measured as 250 kΩ, however, resistance (R) value significantly increased up to 63.2 MΩ after 120 min. under ambient air. On the other hand, in case of remote condition, the R_o value of I_2 doped pPPy films was slightly higher than 1.8 MΩ, but the R value was less increased, compared to that of coupling condition even
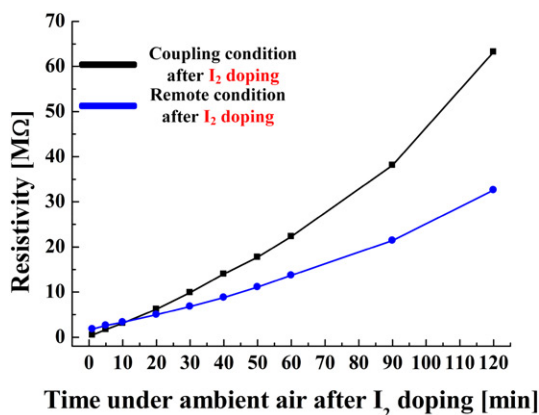
Figure 6. Changes in the resistance of pPPy films of I_2 doped pPPy films after plasma polymerization on interdigitated electrodes relative to exposure time under ambient air.

though the I_2 doping (30 min.) and exposure conditions (*i.e.*, exposed time after I_2 doping process) were exactly the same. Therefore, as shown in XRD, FT-IR, and XPS data, coupling condition, which is influenced by higher energy directly in contact with plasma, has own advantages in terms of crystallinity and chemical structure with abundant multiple bonds, thereby resulting in a lower initial resistance, indicating the possibility as flexible materials. Whereas, the dense and thick I_2 doped APP pPPy films obtained by remote condition were less influenced by hydration under ambient air, thus resulting in showing better stability of resistivity change-rate.

4. Conclusions

In summary, we investigated the structural properties and conductivity characteristics of plasma polymerized conducting polypyrrole by I_2 doping in coupling and remote conditions, respectively. In coupling condition, FT-IR and XPS analyses showed that carbon and nitrogen bonds, such as triple bond $C\equiv C/C\equiv N$ at $2215\,cm^{-1}$ indicating the existence of abundant π-electrons, significantly increased. In addition, XRD analysis exhibited that crystallinity was slightly improved. As a result, I_2 doped APP pPPy film showed better initial resistance of 250 kΩ, compared to that of remote condition. Whereas, in remote condition, the smaller sizes of pPPy particles were densely obtained and formed as a thick film through the I_2 doping process. Furthermore, any remarkable aggregated or vanished APP pPPy features were not observed. From the results, we found that the dense and thick I_2 doped APP pPPy films obtained under remote condition were less influenced by hydration under ambient air, resulting in better stability of resistivity change-rate. Accordingly, these studies of APP pPPy films, which were polymerized under remote and coupling conditions via I_2 doping process, can contribute to providing versatile advantages for future display technologies using flexible electrode-materials.

Acknowledgement

References

[1] Chiang, C. K., Fincher, C. R., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J., Gau, S. C., & MacDiarmid, A. G. (1977). *Phys. Rev. Lett.*, 39, 1098.
[2] Liang, J., Li, L., Niu, X., Yu, Z., & Pei, Q. (2013). *Nat. Photonics*, 7, 817.
[3] Yoon, H. et al. (2013). *Nanomaterials*, 3, 524.
[4] Fernández-Blázquez, J. P., Fell, D., Bonaccurso, E., & Campo, A. D. (2011). *J. Colloid Interface Sci.*, 357, 234.
[5] Kogelschatz, U. et al. (2004). *Plasma Phys. Control. Fusion*, 46, B63.
[6] Dimitrakellis, P., Travlos, A., Psycharis, V. P., & Gogolides, E. (2017). *Plasma Process. Polym.*, 14, 1.
[7] Phan, L. T., Yoon, S. M., & Moon, M.-W. (2017). *Polymers*, 9, 417.
[8] Friedrich, J. et al. (2011). *Plasma Process. Polym.*, 8, 783.
[9] Shi, D., Lian, J., He, P., Wang, L. M., Ooij, W. J. V., Schulz, M., Liu, Y., & Mast, D. B. (2002). *Appl. Phys. Lett.*, 81, 5216.
[10] Wang, J., Neoh, K. G. & Kang, E. T. (2004). *Thin Solid Films*, 446, 205.
[11] Kim, D. H., Park, C.-S., Kim, W. H., Shin, B. J., Hong, J. G., Park, T. S., Seo, J. H., & Tae, H.-S. (2017). *Phys. Plasmas*, 24, 023506.
[12] Park, C.-S., Kim, D. H., Shin, B. J., Kim, D. Y., Lee, H.-K., & Tae H.-S. (2016). *Materials*, 9, 812.
[13] Park, C.-S., Kim, D. Y., Kim, D. H., Lee, H.-K., Shin, B. J., & Tae, H.-S. (2017). *Appl. Phys. Lett.*, 110, 033502.
[14] Kim, D. H., Park, C.-S., Jung, E. Y., Kum, D. S., Kim, J. Y., Kim, D., Bae, G. T., Cho, B.-G., Shin, B. J., Lee, D. H., Chien, S.-I., & Tae, H.-S. (2018). *Mol. Cryst. Liq. Cryst.*, 663, 108.
[15] Cruz, G. J., Olayo, M. G., López, O. G., Gómez, L. M., Morales, J., & Olayo, R. (2010). *Polymer*, 51, 4314.
[16] Goktas, H., Ince, F. G., Iscan, A., Yildiz, I., Kurt, M., & Kaya, I. (2009). *Synth. Met.*, 159, 2001.
[17] Zhang, H., Zhong, X., Xu, J., & Chen, H. (2008). *Langmuir*, 24, 13748.
[18] He, C., Yang, C., & Li, Y. (2003). *Synth. Met.*, 139, 539.