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Synthesis of polyvinylidene fluoride film using novel atmospheric pressure plasma deposition with direct-injection nozzle

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ABSTRACT
This paper proposes a new atmospheric pressure plasma (APP) deposition system with direct-injection nozzle (modified-APPDS) for depositing the polyvinylidene fluoride (PVDF) thin film. In the modified-APPDS, the key parameters such as length of guide-tube, distance of bluff-body, gas composition, and gas flow rates are examined for generating glow-like intense plasma. As a result, the intense glow-like plasma generated broadly by the modified-APPDS can uniformly deposit the PVDF thin film, which is confirmed by field emission-scanning electron microscopy (FE-SEM) and Fourier transforms-infrared spectroscopy (FT-IR).

1. Introduction

Recently, the development trends of display and energy storage devices, will be flexible and portable device with light weight [1–3]. Many previous researches have been mostly investigated on the inorganic materials for flexible devices [3,4]. However, these inorganic materials have some limitations for flexibility and stretchability in the flexible devices. Compared with those inorganic materials, the polymer materials are potential alternatives for flexible devices. The polyvinylidene fluoride (PVDF) is considered as a potential material among many polymers because it has good mechanical flexibility, high chemical resistance, and good thermal stability. In particular, PVDF materials with piezoelectric properties have been recently applied to loudspeakers for flexible displays and force sensing in touch panel [5]. The spin coating, solution casting, and electrospinning are mainly used as a fabrication method of PVDF thin films [6]. However, these conventional methods are not suitable for employing the field of flexible devices, because they are complex, dangerous, and thermal process. Thus, in order to solve these disadvantages, the atmospheric pressure plasma (APP) processes can be effective

method for the deposition of PVDF thin films [7]. In recent, our group has reported a new APP deposition system suitable for depositing the polymer thin film [7,8]. This system tends to lose monomer precursor prior to entering the plasma region for polymerization. Thus, for improving this demerit, it is necessary to separate the part supplying monomer precursor from part producing the Ar plasma. Accordingly, this article proposes the new APP deposition system with direct-injection nozzle (modified-APPDS) for depositing the PVDF thin film. In the modified-APPDS, the length of guide-tube, distance of bluff-body, gas composition (only He gas and Ar-He gas mixtures), and gas flow rates are examined as the key parameters for generating glow-like intense plasma. The discharge characteristics of the modified-APPDS are investigated by using digital single lens reflex (DSLR) camera, intensified charge-coupled device (ICCD), and optical emission spectroscopy (OES) as a function of key parameters. In addition, the characteristics of PVDF thin film deposited by the modified-APPDS are investigated by using scanning electron microscopy (SEM) and Fourier transforms-infrared spectroscopy (FT-IR).

2. Experiments

To make a PVDF solution with a concentration of 5%, a total of 1.95 g of PVDF powder (Sigma-Aldrich) was dissolved in a mixture with 40 ml dimethylformamide (DMF; DaeJung Chemicals Ltd.) solution. In order to efficiently dissolve the PVDF powder into a mixture without agglomeration during the dissolution process, a magnetic stirrer with angular velocity of 500 rpm was used with hotplate at 40 °C for 24 h. The PVDF solution was coated on glass substrate by the modified APP deposition system with direct-injection nozzle (modified-APPDS). Figure 1 showed a schematic diagram of the modified-APPDS used in this study. The APP system without direct-injection nozzle was described in detail by C-S Park et.al. [7,8]. The modified-APPDS consisted of a quartz guide-tube, polytetrafluoroethylene bluff-body, and direct-injection nozzle. Both inner diameter of guide-tube and outer diameter of guide-tube had a 20 mm and 15 mm, respectively. Moreover, the direct-injection nozzle of quartz-tube was connected to the side of guide-tube. In addition, in case of direct-injection nozzle, inner and outer diameter of quartz-tube were about 1 mm and 3 mm, respectively. The high purity of Argon (99.999%) and He (99.999%) gases were used as a main gas for producing the plasma. PVDF solution was vaporized using a glass bubbler, which was supplied by argon gas with a flow rate of 300 standard cubic centimeters per minute (sccm). The sinusoidal power with a peak value of 10 kV and a frequency of 26 kHz was applied to the powdered electrode for producing the plasma. The characteristics of plasma produced by the modified-APPDS strongly depend on the system configuration, gas composition, and gas flow rates. Accordingly, in order to produce the glow-like intense plasma suitable for the deposition of PVDF thin film, four case studies shown in Fig. 1 are carried out in these experiments. The detailed plasma conditions for deposition were given in Table 1. Photo images of the glow discharge and plasma plumes were obtained with a DSLR camera (Nikon, D56300) and ICCD (Princeton Instruments, 7476-0017). To verify the excited reactive radical species such as reactive nitrogen
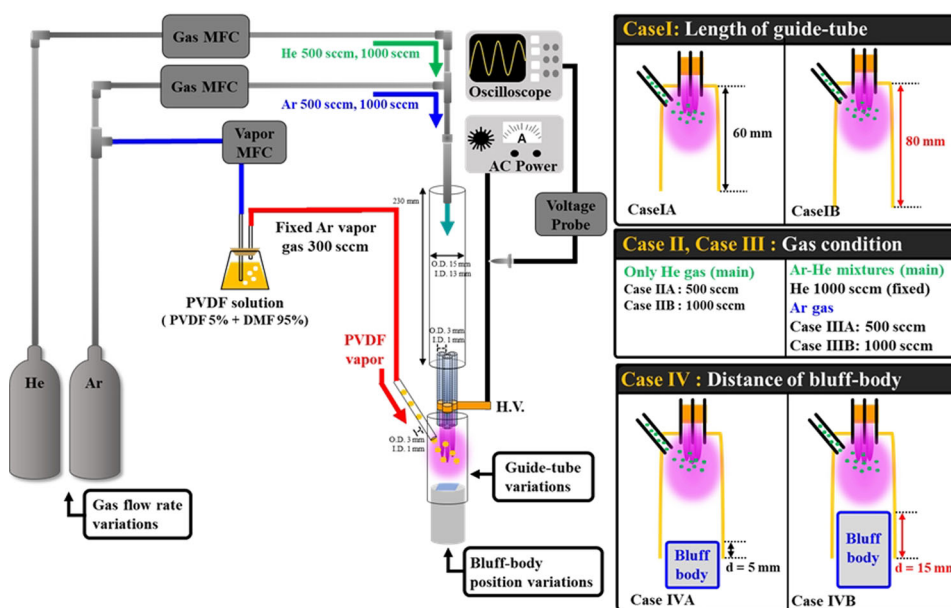
Figure 1. Schematic diagram of the modified APP deposition system with direct-injection nozzle (modified-APPDS) used in this study.

Table 1. The plasma conditions for generating the glow discharge and deposition conditions of polyvinylidene fluoride (PVDF) thin film prepared by the modified APP deposition system with direct-injection nozzle (modified-APPDS).

Experimental Parameters		Unit	Experimental Conditions
Discharge	Ar Flow Rate (PVDF line)	[sccm]	300
	Ar Flow Rate (Main line)	[sccm]	500 / 1000
	He Flow Rate	[sccm]	500 / 1000
	Applied Voltage	[kV]	10
	Power Frequency	[kHz]	26
Deposition	Deposition Time	[h]	1
	Substrate Temperature	[°C]	Room Temp.
	Pre-heating Temperature	[°C]	60
	Pre-heating Time	[h]	0.5
	Post-heating Temperature	[°C]	160
	Post-heating Time	[h]	0.5

species (RNS) and excited Ar radicals, the optical emission spectra were acquired from the optical emission spectrometer (OES; Ocean Optics USB-4000UV-VIS).

In order to remove the DMF within the PVDF thin film deposited by the modified-APPDS, the PVDF thin film was heated on a hotplate with a two-step heating process. The first step was removing the solvent of DMF at 60 °C for 0.5-h and second step was a post-heating process at 160 °C for 3-h in order to form the crystalline phase of PVDF thin film. The detailed deposition conditions of PVDF thin film were given in Table 2. The surface morphology images and film thickness of PVDF thin films were examined by using scanning electron microscope (SEM; Hitachi SU8220) and stylus profiler (KLA Tencor, P-7), respectively. The crystalline phases of PVDF thin film were measured by Fourier transformation infrared spectroscopy (FT-IR; Vertex 70, Bruker). The FT-IR

Table 2. The detailed case studies for generating the glow discharge with intense cloud-like plasma of the modified-APPDS used in this study.
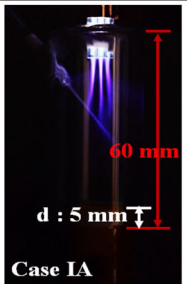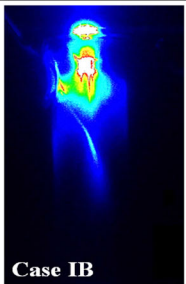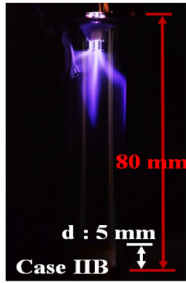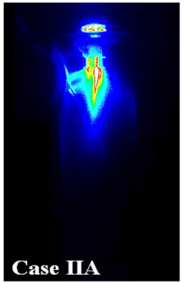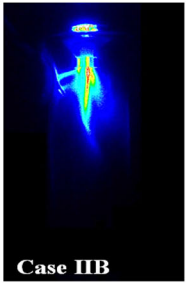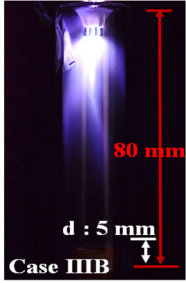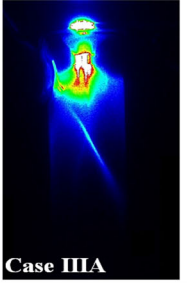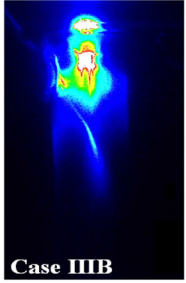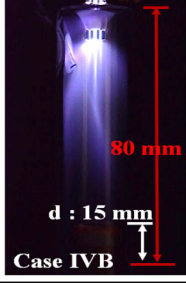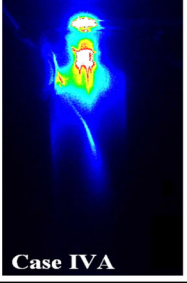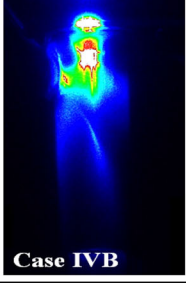
	Length of guide-tube	He main gas flow	Ar main gas flow	Distance of bluff-body
Case I	Case IA: 60 mm Case IB: 80 mm	1000 sccm	1000 sccm	5 mm
Case II	80 mm	Case IIA: 500 sccm Case IIB: 1000 sccm	0 sccm	5 mm
Case III	80 mm	1000 sccm	Case IIIA: 500 sccm Case IIIB: 1000 sccm	5 mm
Case IV	80 mm	1000 sccm	1000 sccm	Case IVA: 5 mm Case IVB: 15 mm

spectra were measured by averaging 128 scans at a wavenumber resolution of $0.6\,cm^{-1}$ in the range from $600\,cm^{-1}$ to $4000\,cm^{-1}$ using attenuated total reflection (ATR) mode.

3. Result and discussion

Figure 2 shows the photo and ICCD images of discharge formed by the modified-APPDS with respect to various case studies such as length of guide-tube (case IA and case IB), only He gas flow rates (case IIA and case IIB), Ar gas flow rates (case IIIA and case IIIB), and distance of bluff-body (case IVA and case IVB). In order to optimize the geometry of plasma device for deposition, we investigated the two cases, na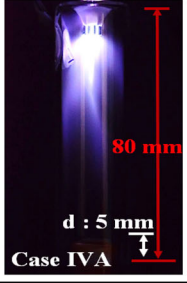mely, length of guide-tube of 60 mm (case IA) and 80 mm (case IB) when the bluff body was positioned at 5 mm inside guide-tube with Ar-He gas mixtures (Ar 1000 sccm and He 1000 sccm). As shown in Fig. 2, in case of case IA, the plasma was produced in the form of only plasma plumes and each plasma plume was not merged together. For case IB, the three plasma plums were well merged together, thus forming highly intense cloud-like uniform plasma in the guide-tube. This result confirmed that the optimal length of guide-tube was required to generate the glow discharge with intense cloud-like plasma for deposition. For He gas flow rate cases (case IIA: 500 sccm and case IIB: 1000 sccm), other system configurations were fixed; length of guide-tube of 80 mm and the insertion distance of bluff body from the end of guide-tube. In cases IIA and IIB, the plasma was weakly merged thus forming weak plasma in the guide-tube. For Ar gas flow rate cases (case IIIA: 500 sccm and case IIIB: 1000 sccm), other conditions were fixed; length of guide-tube of 80 mm, the insertion distance of bluff body from the end of guide-tube, and He gas flow of 1000 sccm under Ar-He gas mixtures. As shown in Fig. 2, when increasing the Ar gas flow rates from 500 sccm (case IIIA) and 1000 sccm (case IIIB), the produced plasma was observed to be highly intense cloud-like plasma, compared to the only He gas (cases IIA and IIB). This result implies that the higher Ar gas has an important role in generating the glow discharge with highly intense cloud-like glow plasma [9,10,13]. When changing the distance of bluff-body from 5 mm (case IVA) to 15 mm (case IVB) under the other same conditions, the produced plasma was observed to be a little intense cloud-like plasma, as shown in Fig. 2 (case IV). In Fig. 2, cases IB, IIIB, and IVA were exactly the same in this study.

To investigate the mechanism of the produced plasma with intense cloud-like and effect of the excited reactive radical species produced using Ar with He gas discharge by the modified-APPDS, optical emission spectroscopy (OES) measured the excited reactive radical species such as reactive nitrogen species (RNS), reactive oxygen species (ROS),

Conditions	Photo images		ICCD images	
Case I	Case IA 60 mm d : 5 mm	Case IB 80 mm d : 5 mm	Case IA	Case IB
	Guide-tube : 60 mm	Guide-tube : 80 mm	Guide-tube : 60 mm	Guide-tube : 80 mm
Case II	Case IIA 80 mm d : 5 mm	Case IIB 80 mm d : 5 mm	Case IIA	Case IIB
	He : 500 sccm	He : 1000 sccm	He : 500 sccm	He : 1000 sccm
Case III	Case IIIA 80 mm d : 5 mm	Case IIIB 80 mm d : 5 mm	Case IIIA	Case IIIB
	Ar 500 sccm	Ar 1000 sccm	Ar 500 sccm	Ar 1000 sccm
Case IV	Case IVA 80 mm d : 5 mm	Case IVB 80 mm d : 15 mm	Case IVA	Case IVB
	d : 5 mm	d : 15 mm	d : 5 mm	d : 15 mm

Figure 2. Photo images and ICCD images of plasmas produced in the modified-APPDS with respect to various case studies such as length of guide-tube (case IA and case IB), gas compositions (case IIA and case IIB), Ar gas flow rates (case IIIA and case IIIB), and distance of bluff-body (case IVA and case IVB).
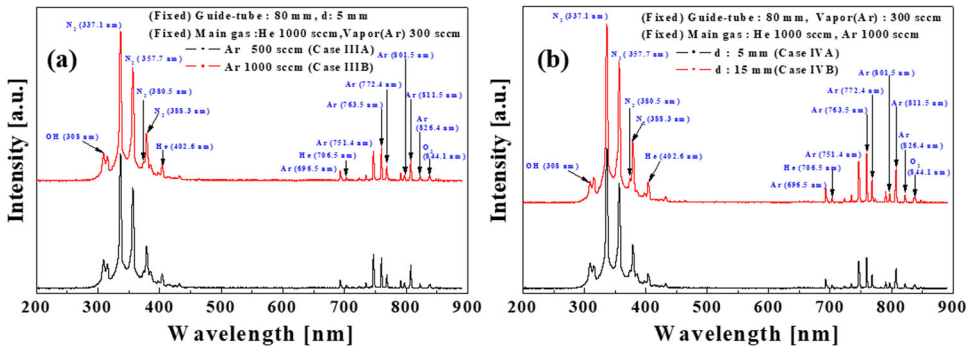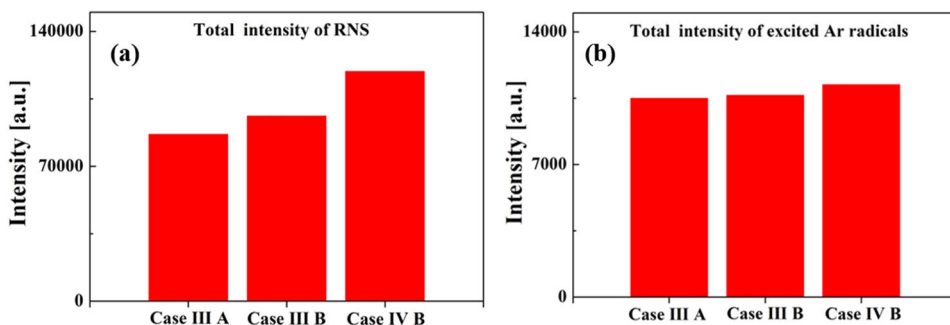
Figure 3. Optical emission spectroscopy (OES) spectra of the modified-APPDS with respect to various case studies such as Ar gas flow rates (case IIIA and case IIIB) and distance of bluff-body (case IVA and case IVB) when the length of guide-tube was at 80 mm with He gas flow rate of 1000 sccm and Ar gas flow for vaporing is fixed at 300 sccm.

and excited Ar radicals in the nucleation region of the modified-APPDS. Figure 3 shows the OES spectra of the plasma produced in the modified-APPDS for four cases(cases IIIA, IIIB, IVA, and IVB). As shown in Fig. 3, several peaks of excited N_2, OH, He, O and Ar were observed in the OES data. The N_2 and oxygen species peaks exhibited a RNS and ROS, respectively. RNS peaks are related to the wavelength ranging from 330 nm to 388 nm, whereas ROS peaks are related to the wavelengths at 308 nm and 844.1 nm. The excited Ar radicals are related to the wavelength ranging from 695 nm to 850 nm [9,10,13]. In Fig. 3a, when increasing the Ar gas flow rates from 500 sccm (case IIIA) to 1000 sccm (case IIIB), the peak intensities of RNS and excited Ar radicals increased, which resulted from a frequent collision reaction between gas mixtures. These results mean that the increase of the excited radical species contributes to the fragmentation and recombination for obtaining the PVDF thin film [9,10]. In Fig. 3b, when changing the distance of bluff-body from 5 mm (case IVA) to 15 mm (case IVB), the peak intensities of RNS and excited Ar radicals also increased, which resulted from suppressing the inflow of ambient air into the plasma region [9].

To compare the OES analysis quantitatively among the RNS and excited Ar radicals, the total emission intensities are calculated from each emission intensity. Figure 4a and b shows the total peaks intensities of RNS and excited Ar radicals were calculated from OES spectra of Figure 3a and b, respectively. The total peaks intensities of RNS in Fig. 4) mean the sum of peak intensity of several RNS obtained from the OES spectra of Fig. 3a and b where the wavelengths of several RNS are 337.1, 357.7, 380.5, and 388.3 nm. The total peaks intensities of exited Ar radicals in Fig. 4b mean the sum of peak intensity of several exited Ar radicals obtained from the OES spectra of Fig. 3a and b where the wavelengths of several exited Ar radical are 696.5, 751.4, 763.5, 772.4, 801.5, 811.5, and 826.4 nm. The increase in the total peaks intensities of RNS and excited Ar radicals is related to an amount of Ar gas flow rate including the position of the bluff-body that the substrate is placed on. Based on the experimental results of Figures 2–4, the optimal deposition conditions were chosen for the synthesis of the PVDF thin film.

In order to investigate the morphology and crystalline phase of PVDF thin film deposited by the proposed APP deposition system with optimal condition (case IVB),

Figure 4. Total peak intensity of excited RNS and Ar radicals from OES spectra for the modified-APPDS with respect to various conditions such as Ar gas flow rates (case IIIA and case IIIB) and distance of bluff-body (case IVB) from OES spectra in Figure 3 when the length of guide-tube was at 80 mm with He gas flow rate of 1000 sccm and Ar gas flow for vaporing is fixed at 300 sccm.
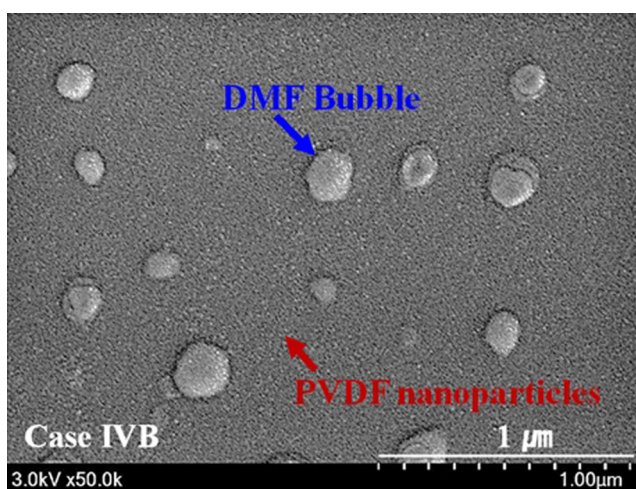

Figure 5. Scanning electron microscopy (SEM) image of PVDF thin film prepared by the modified-APPDS with optimal condition (case IVB).

the deposited PVDF thin films were post-heated on hotplate at $160\,^{\circ}$C for 3-h. The morphology and crystalline phase of the deposited PVDF thin film were measured by FE-SEM and FT-IR. Figure 5 shows the FE-SEM images of the deposited PVDF thin films prepared by the modified-APPDS with optimal condition (case IVB). The thickness of the grown PVDF thin film was measured to be about $1\,\mu$m by using stylus profiler. As shown in Figure 5, the bubbles attached on the deposited PVDF thin film was observed, which was originated from DMF solution. The dense surface of the PVDF thin film was observed, and the dense surface consisted of nanoparticles.

Figure 6 shows the FT-IR spectra of PVDF thin film prepared by the modified-APPDS with optimal condition (case IVB). As shown in Fig. 6, the peaks at $975\,\mathrm{cm}^{-1}$ and $1402\,\mathrm{cm}^{-1}$ were assigned to α-phase, and peak at $1072\,\mathrm{cm}^{-1}$ was assigned to β-phase, which confirmed that the grown film was PVDF thin film. The absorption peaks of DMF solution originally had two characteristics bands at $1032\,\mathrm{cm}^{-1}$ and
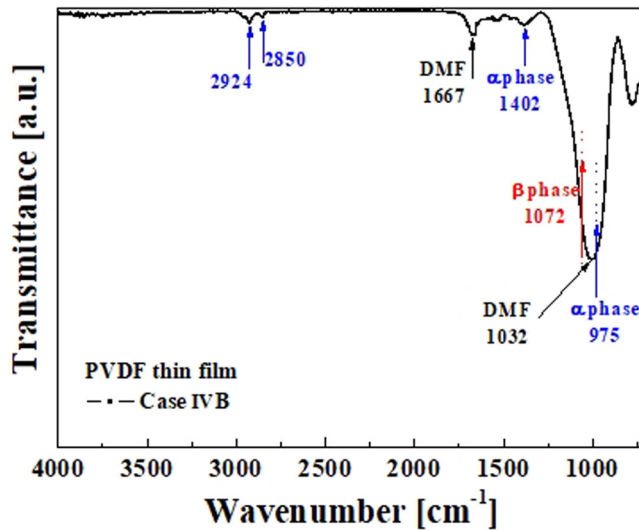
Figure 6. Fourier transformation infrared spectroscopy (FTIR) spectra of PVDF thin film prepared by the modified-APPDS with optimal condition (case IVB).

$1667 \, cm^{-1}$, which were assigned to -C-N and -C$=$O bonds, respectively [5,16]. As a result, the crystalline phase of PVDF thin film prepared by the modified-APPDS mainly had two phases of α- and β-phases in FTIR spectra.

4. Conclusions

In summary, in order to minimize the loss of monomer precursor and a contamination for the APP system, this article proposes the modified-APPDS for depositing the PVDF thin film. In the modified-APPDS, the length of guide-tube, distance of bluff-body, gas composition (only He gas and Ar-He gas mixtures), and gas flow rates were examined as the key parameters for generating glow-like intense plasma. The glow-like intense plasma was produced at an optimal condition of case IVB, which was confirmed by ICCD and OES. In particular, OES spectra showed that the excited reactive radical species were increased by collision reaction between gas particles at the optimal condition of case IVB. The morphology and crystalline phase of the PVDF thin film deposited at the optimal condition of case IVB were examined by FE-SEM and FT-IR. Therefore, Thus, PVDF thin film was successfully deposited with a thickness of $1 \, \mu m$ by the modified-APPDS, which was confirmed by the two phases of α- and β-phases of FT-IR. This method is expected to be a low cost and simple process for depositing the polymeric thin film in the field of flexible devices.

Funding

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