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Influences of guide-tube and bluff-body on advanced atmospheric pressure plasma source for single-crystalline polymer nanoparticle synthesis at low temperature

Dong Ha Kim,1,a) Choon-Sang Park,1,a) Won Hyun Kim,2 Bhum Jae Shin,3 Jung Goo Hong,2 Tae Seon Park,2 Jeong Hyun Seo,4 and Heung-Sik Tae1,b)

1School of Electronics Engineering, College of IT Engineering, Kyungpook National University, Daegu 702-701, South Korea
2School of Mechanical Engineering, College of Engineering, Kyungpook National University, Daegu 702-701, South Korea
3Department of Electronics Engineering, Sejong University, Seoul 143-747, South Korea
4Department of Electronics Engineering, Incheon National University, Incheon 406-772, South Korea

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The use of a guide-tube and bluff-body with an advanced atmospheric pressure plasma source is investigated for the low-temperature synthesis of single-crystalline high-density plasma polymerized pyrrole (pPPy) nano-materials on glass and flexible substrates. Three process parameters, including the position of the bluff-body, Ar gas flow rate, and remoteness of the substrate from the intense and broadened plasma, are varied and examined in detail. Plus, for an in-depth understanding of the flow structure development with the guide-tube and bluff-body, various numerical simulations are also conducted using the same geometric conditions as the experiments. As a result, depending on both the position of the bluff-body and the Ar gas flow rate, an intense and broadened plasma as a glow-like discharge was produced in a large area. The production of the glow-like discharge played a significant role in increasing the plasma energy required for full cracking of the monomers in the nucleation region. Furthermore, a remote growth condition was another critical process parameter for minimizing the etching and thermal damage during the plasma polymerization, resulting in single- and poly-crystalline pPPy nanoparticles at a low temperature with the proposed atmospheric pressure plasma jet device.

I. INTRODUCTION

Due to various advantages, such as low cost1–6 and low-temperature dry process features,7–15 atmospheric pressure plasma jets (APPJs) are a promising growth source for the deposition of plasma polymer films16–20 with functional properties that are well-suited for a wide range of substrates and applications.14,21,22 Plasma polymer films grown using plasma sources such as low-pressure and radio-frequency (RF) plasmas are known to be pinhole-free, highly cross-linked, insoluble, branched, and adherent to various substrates.23–31 Nonetheless, to obtain high-quality polymer thin films using plasma sources, especially APPJs, the following difficulties need to be overcome. First, conventional APPJs are unable to feed enough energy for nucleation and activation of the monomers due to the weak plasma energy in atmospheric air.32–35 Second, depending on the size of the APPJ device, especially single jets, the plasma jet diameter is typically only a few millimeters, meaning that the processing area is limited and unsuitable for large-area polymerization.35,36 Third, the use of argon (Ar) gas is more beneficial for large-scale applications of plasma jet arrays.37–39 However, Ar plasma jet arrays are difficult to control due to their high breakdown voltage, easy glow-to-arc transition, and heavier atom mass.40,41 Finally, understanding the interaction between the plasma and the substrate is critical for suppressing plasma damage during plasma polymerization.42–44

Thus, to ensure that the monomers are completely fragmented in the discharge region, it is important to increase the plasma energy by suppressing the inflow of ambient air into the process region; that is, an Ar-rich condition is required to enhance the plasma energy in the process region for efficient fragmentation of the monomers. Furthermore, the position of the substrate for growing polymer thin films needs to be considered in relation to the intense plasma region; that is, a remote substrate location is required to avoid severe plasma damage induced by energetic charged particles.

The current authors recently reported a new polymer synthesis method using a novel APPJ device, where polycrystalline plasma-polymerized aniline (pPANI) nanomaterials were successfully grown under Ar dominant gas conditions by simply shielding the plasma generation region from the ambient air.45 However, to understand the detailed growth mechanism of high-quality polymer polymers when using high-pressure plasma jets, the plasma polymerization process and numerical procedure of gas fluid physics need to be investigated when varying several critical parameters, such as the position of the polytetrafluoroethylene (PTFE)
bluff-body (hereinafter, bluff-body) in the glass tube, gas flow rate (or gas velocity), and electrical interaction of the plasma plume with the surface of the substrate.

Accordingly, this study experimentally and numerically examined the effects of the guide-tube and bluff-body on an advanced APPJ device for the low-temperature synthesis of high-density plasma-polymerized pyrrole (pPPy) with a single-crystalline characteristic. Thus, we examined the effects of three process parameters on generating a uniform and strong glow-like discharge in the proposed APPJ device for large-area treatment and improving the crystalline characteristic of pPPy. The three process parameters were the position of the bluff-body with respect to the guide-tube, the Ar gas flow rate, and the remoteness of the substrate from the intense and broadened plasma. The gas fluid and plasma characteristics were measured using numerical procedures, optical emission spectroscopy (OES), infrared spectroscopy (IR), and the currents. Fourier transform infrared spectroscopy (FT-IR), field emission-scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM) were also used to analyze the pPPy nano-materials.

The experimental results showed the production of unique plasma characteristics in the nucleation region of the advanced APPJs, that is, the streamer-like discharge or glow-like discharge varied considerably depending on both the position of the bluff-body with respect to the guide-tube and the Ar gas flow rate. Moreover, the crystalline quality of the pPPy grown using the advanced APPJs depended strongly on the remoteness of the substrate from the uniform and intensified glow-like discharge.

II. EXPERIMENTAL

Figure 1 shows a schematic diagram of the experimental setup of the advanced APPJs used in this study. 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. The center-to-center distance between two adjacent tubes was exactly 3 mm. As shown in Figure 1, one of the critical components of the proposed APPJs is the glass guide-tube (hereinafter, guide-tube), constituting the nucleation region where the pyrrole monomers are cracked by the Ar plasma. Here, the guide-tube was 60 mm in length, with an inner diameter of 20 mm. Another critical component is the bluff-body, as the position of the bluff-body with respect to the guide-tube has a significant influence on whether intense and broadened plasma can be produced in the nucleation region. Here, the bluff-body had an outer diameter of 15 mm. The substrates employed for the plasma polymerization included glass, Si wafers, and polyethylene terephthalate (PET). The substrates were mounted on the bluff-body. High purity Ar gas (99.999%) was used as the discharge gas for the plasma generation, and its flow rate was varied from 700 to 1600 standard cubic centimeters per minute (sccm) at an interval of 300 sccm. The liquid pyrrole monomer (Sigma-Aldrich Co., St. Louis, Missouri, USA, Mw = 67 g mol\(^{-1}\)) was vaporized using a glass bubbler that supplied the Ar gas at a flow rate of 130 sccm. A sinusoidal power source was connected to the powered electrode via a driving circuit with a peak value of 12 kV and a frequency of

![Schematic diagram of the experimental set-up employed in this study.](https://example.com/schematic_diagram.png)
30 kHz. A high-voltage probe (Tektronix P6015A) and current probe (Pearson 4100) were connected between the power source via an inverter circuit and oscilloscope (LeCroy WaveRunner 64Xi) to measure the applied voltage and total current, respectively. In the driving circuit, the inverter amplified the low primary voltage to reach a high secondary voltage. As a result, the driving circuit generated a sinusoidal voltage of several tens of kilovolts, with a frequency of several tens of kilohertz. A photo-sensor amplifier (Hamamatsu C6386-01) was employed to analyze the plasma infrared (IR) emission in the nucleation region. The wavelength-unresolved optical emission waveform from the photo-sensor amplifier with a range of 400–1100 nm (middle range) was connected to an oscilloscope. A 1-mm-thick glass sheet was placed in front of the photo-sensor amplifier to eliminate any external signals. Since the measurement lead of the optical fiber was attached just below the substrate, the measured plasma infrared (IR) intensity varied depending on the remoteness of the substrate from the plasma plume.

All the photographs of the devices and plasma plumes were taken using a DSLR camera (Nikon D5300) with a Macro 1:1 lens (Tamron SP AF 90 mm F2.8 Di). An optical emission spectrometer (OES, Ocean Optics, USB-4000UV-VIS) was used to identify the diverse reactive species in the plasma. Instead of measuring the plasma density and electron temperature, a photo-sensor amplifier and OES techniques were used to measure and analyze the optical intensities and spectra of the reactive nitrogen/oxygen peaks, respectively, to estimate the variations in the plasma energy. Before the plasma polymerization, the substrates with identical sizes of 10 mm × 10 mm were ultra-sonically cleaned in 99.99% acetone, isopropanol, and distilled (DI) water for 20 min, respectively, to remove any contaminants from the surface of the substrates. The surface temperature of the substrates was measured using a special glass tube with an infrared thermometer (Fluke, 568 IR Thermometer).

The study investigated the effects of varying three process parameters to enable the advanced array APPJs to produce broadly distributed intense glow-like plasmas for large-area treatment. Based on the optimized results for the proposed APPJ, the optimized growth process conditions were identified for high-quality plasma polymer thin films, that is, the conditions were optimized for improving the crystalline quality of the plasma polymer thin films. The detailed process parameters are given in Figure 2(a) and Table I. To investigate the blocking effect of the bluff-body, the first process parameter involved varying the position of the bluff-body with respect to the guide-tube at a constant Ar gas flow rate of 1300 sccm; that is, in case I, the bluff-body was located outside the guide-tube, in case II, the bluff-body was located exactly at the end of the guide-tube, and in cases III–V, the bluff body was located inside the guide-tube. The second process parameter involved varying the Ar gas flow rate from 700 to 1600 sccm at an interval of 300 sccm for case III, where the bluff-body was located about 5 mm inside the guide-tube: that is, all the other experimental conditions were exactly the same as those for case III, except for the Ar gas flow rate.

Figure 2(b) shows a cross-sectional schematic diagram of the three jets and guide-tube comprising the proposed APPJs for large-area treatment. In the case of conventional APPJs without a guide-tube or bluff-body, the plasma is only produced within the area of the three array jets (or bundle of 3 glass tubes) due to the directional characteristic of the streamer-like discharge. However, in our previous study, the streamer-like plasma was already proven to be unsuitable for growing high-quality plasma polymer thin films. In contrast, with the proposed APPJs, the plasma produced in the nucleation region can be transited from a narrow streamer-like discharge into a broadened glow-like discharge by properly adjusting the process parameters. Importantly, when producing the broader glow-like plasma in the nucleation region, the plasma area is dramatically enlarged (about 60-fold increase) when compared with that with the narrow streamer-like plasma produced by conventional APPJs with three arrays. Plus, the experiments showed that the proper combination of the guide-tube with the bottom played a significant role in producing largely distributed glow-like plasma in the nucleation region, thereby also improving the crystalline quality of the plasma polymer thin films.

Figure 3 shows the changes in the plasma images produced in the nucleation region when varying the process parameters. As shown by case I in Figure 3(a), the short plasma plumes produced in the limited region looked like the streamer discharge typically observed with conventional array jets. In case II, the plasma plume still appeared to be a streamer discharge, even though its intensity was slightly enhanced and its length slightly extended compared to that of case I. However, in case III, where the bluff-body was located inside the guide-tube, strong plasma plumes were produced and extended much farther downstream, confirming that the conditions of case III caused a dramatic transition of the plasma produced from a narrow streamer-like discharge into a broadened and intense glow-like discharge. Thus, the proper combination of the bluff-body with the guide-tube provided Ar-rich conditions that increased the plasma energy in the nucleation region by suppressing the inflow of ambient air into the plasma production region. As a result of minimizing the quenching effect, an intensified glow-like plasma cloud was produced, as shown by case III in Figure 3(a).

Figure 3(b) shows the plasma images produced in the nucleation region of the proposed APPJs according to the Ar gas flow rate under the process parameter conditions of case III. In the case of a low gas flow rate below 1300 sccm (i.e., case III A: 700 sccm and case III B: 1000 sccm), no intense or broadened plasma was produced even though the bluff-body was located inside the guide-tube. Meanwhile, when the gas flow rate was over 1300 sccm (i.e., case III C: 1300 sccm and case III D: 1600 sccm), the intense and broadened plasma was produced in case III when the bluff-body was located inside the guide-tube. This result shows that the Ar gas flow rate was also a significant process parameter for producing intense glow-like plasma. In other words, increasing the Ar gas flow rate under the conditions of case III increased the Ar species and monomers in the nucleation region, resulting in an intense glow-like discharge that is needed for fully cracking the monomers in the nucleation
Moreover, to avoid thermal and etching damage, the substrate needs to be located away from the intense plasma region during the plasma polymerization. Thus, cases IV and V in Figure 3(c) and Table I were used to check the effect of another process parameter as regards minimizing the plasma damage during plasma polymerization. In cases IV and V, as the substrate approached the intense plasma region, more intense glow-like plasmas were produced, yet additional streamer-like discharges were also observed in the immediate vicinity of the substrate, as shown in Figure 3(c). Direct contact between the substrate and the plasma plume can cause thermal damage or etching, eventually aggravating the quality of the polymer films grown in the APPJs.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Parametric cases</th>
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</thead>
<tbody>
<tr>
<td>Position of bluff body (distance from end of guide-tube) (Ar gas flow rate: 1300 sccm)</td>
<td>(Case I) Outside 5 mm (Case II) 0 mm (Case III) Inside 5 mm (Case IV) Inside 25 mm (Case V) Inside 40 mm (Case III A) Ar 700 sccm (Case III B) Ar 1000 sccm (Case III C) Ar 1300 sccm (Case III D) Ar 1600 sccm</td>
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<tr>
<td>Gas flow rate (under case III)</td>
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<td>(Case III A)</td>
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<td>(Case III B)</td>
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<td>(Case III C)</td>
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<td>(Case III D)</td>
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*Note that case III and case III C are exactly the same experimental condition.
Consequently, unlike cases IV and V (non-remote condition or coupling condition), case III (=case III C) represents a remote mode that is suitable for the efficient deposition of plasma polymerized nanoparticles without etching or thermal damage.

**III. RESULTS AND DISCUSSION**

**A. Numerical procedure and results**

To gain an in-depth understanding of the flow structure development within the guide-tube and bluff-body, various numerical simulations were also conducted using the same geometric conditions as the experiments. Herein, while the numerical simulations only depict the non-plasma flow field, the plasma added flow behavior can be inferred on the basis of available computational results.

Figure 4 shows the entire computational domain with the geometric conditions, including three main parts: the inflow tube, mixing chamber, and bluff-body, corresponding to the bundle of three glass tubes, guide-tube, and bluff-body in the experiments, respectively. To determine the effects of the inserted bluff-body on the flow structure, five bluff-body positions from the outlet were selected, similar to the experimental conditions of cases I–V. The incoming fluid into the
mixing chamber (guide-tube) was prescribed as a perfectly stirred mixture of Ar (1300 sccm) and the Ar + monomer (130 sccm) with 300 K ejecting from the inflow tube (bundle of three jets). The details of the geometric and boundary conditions are summarized in Table II. As plotted in Figure 4, the current geometric feature was very similar to a small-scale dump or can-type combustor. According to previous studies of such meso- or micro-scale combustors, a turbulence model is recommended to obtain more accurate numerical results than assuming a laminar flow regime when the Reynolds number is more than 400.50–52 In the present study, the Reynolds number based on the inflow tube diameter (D_t) was about 700. Moreover, not referred in this paper, an unsteady simulation was performed and the results were compared with the steady simulation. As a result, since the unsteadiness of the flow feature was determined to be very weak, the numerical simulations were only conducted for steady and incompressible turbulent flows, and the governing equation for the continuity and momentum is as follows:

\[
\frac{\partial}{\partial x_i} (\rho u_i) = 0, \quad (1)
\]

\[
\frac{\partial}{\partial x_j} (\rho u_i u_j) = - \frac{\partial P}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} - \frac{\partial}{\partial x_j} \left( \rho w_i u_j \right), \quad (2)
\]

where \( \rho, u_i, P, \tau_{ij}, \) and \( w_i u_j \) denote the density, velocity components, pressure, stress tensor, and Reynolds stress, respectively. When using Ansys FLUENT 13.0,53 the SIMPLEC Algorithm was applied for the pressure-velocity coupling and the second-order upwind scheme used for all the equations. In Equation (2), the turbulent fluctuation driven Reynolds stress term \( (\overline{w_i u_j}) \) required additional modelling to solve the turbulent flows. As various turbulent models are available, selecting the proper turbulence model is crucial to achieve an exact prediction of the turbulent flows. Moreover, due to a sudden expansion of the volume, recirculating flows occur in the dump region. Such characteristic flow features are mainly induced by the high strain rate and pressure gradient intensifying with the help of turbulence anisotropy. Thus, to obtain an exact solution, the anisotropy of Reynolds stress must be considered. Therefore, this study applied the Reynolds stress model (RSM) among the various turbulence approaches and the transport equation for Reynolds stress is expressed as follows:53

\[
\frac{\partial}{\partial x_i} \left( \rho u_i \overline{u_i u_j} \right) = D_{ij} + P_{ij} + \phi_{ij} + \varepsilon_{ij}, \quad (3)
\]

where \( D_{ij}, P_{ij}, G_{ij}, \phi_{ij}, \) and \( \varepsilon_{ij} \) denote the turbulent diffusion, stress production, pressure strain, and dissipation term, respectively. The modelling details for each term and the model constants have been omitted.53

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**TABLE II. Details of geometric and boundary conditions for numerical simulation.**

<table>
<thead>
<tr>
<th>Geometric conditions</th>
<th>1.5 mm</th>
<th>3 mm</th>
<th>20 mm</th>
<th>6 mm</th>
<th>9 mm</th>
<th>7.5 mm</th>
<th>60 mm</th>
<th>10 mm</th>
<th>Outside 5 mm (case I)</th>
<th>0 mm (case II)</th>
<th>Inside 5 mm (case III)</th>
<th>Inside 25 mm (case IV)</th>
<th>Inside 40 mm (case V)</th>
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<tr>
<td>D_i (inner jet diameter)</td>
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<td>D_o (outer jet diameter)</td>
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<td>D_t (inflow tube diameter)</td>
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<td>d (distance between jet centers)</td>
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<td>r_b (bluff-body radius)</td>
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<td>L_t (inflow tube length)</td>
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<td>L_b (bluff-body position from outlet)</td>
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<tr>
<th>Boundary conditions</th>
<th>Velocity inlet, 300 K (Ar+ monomer mixtures, 5.864 m/s)</th>
<th>Pressure outlet, 300 K</th>
<th>Solid wall, 300 K</th>
<th>Glass, 300 K</th>
<th>Glass, 300 K</th>
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<tbody>
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<td>Inlet</td>
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<td>Outlet</td>
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<td>Bluff-body</td>
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<td>Inflow tube wall</td>
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<td>Mixing chamber wall</td>
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To validate the use of the present numerical method, the comparable results between the RSM and the experiment for the jet plumes of case I are plotted in Figure 5. As shown, the jet plumes of the numerical results are described by the iso-surface of $U/U_m = 0.4$ where $U_m$ is the mean streamwise velocity of a single jet exit. Although the numerical results of the RSM represent a non-plasma flow condition, the predicted jet plumes of the RSM agreed well with the experimental results. This feature confirmed that the RSM was very effective in describing the flow structure in the mixing chamber.

To check the grid dependency, four grid resolutions were tested before any further numerical simulations. For comparison, the distribution of the streamwise velocity on the center axis with the streamline contour of the $x$-$z$ plane at $y/D_o = 0.288$ is presented in Figure 6. When the number of control volumes (CVs) was more than 600,000, the discrepancy depending on the grid resolution for the streamwise velocity distribution and the formation of recirculating flows was negligible. Therefore, the grid resolutions in the present study were maintained at about 650,000–700,000 CVs.

Figure 7 shows the distribution of the streamwise velocity ($U/U_c$) at the jet center axis with the streamline contour of the $x$-$z$ plane at $y/D_o = 0.288$ for different bluff-body positions ($L_b$), where $U_c$ is the streamwise velocity of a jet center at the inflow exit plane. Regardless of $L_b$, a steep decrease of $U/U_c$ was observed for $0 < x/D_o < 3.0$ due to a sudden expansion of the volume. Thereafter, $U/U_c$ gradually decayed as the flow developed downstream. Because of the momentum difference between the incoming mixture and the ambient fluids near the dump region, a wallward motion of recirculating flows occurred in all cases. Herein, it is worth noting that the decline pattern of $U/U_c$ and development of recirculating flows for cases II and III were roughly identical to case I without the bluff-body. Those cases had recirculating flows for $x/D_o = 15.0$ to a certain distance apart from the bluff-body. This means there was no mutual effect between the bluff-body and the flow recirculation zones. Thus, the flow structures for cases I–III developed alike. Conversely, the bluff-body had a definite effect on the development of the flow structure in cases IV and V. Namely, confined and deformed recirculating flows arose when the bluff-body was...
located further upstream. This was mainly due to insufficient space for fully developed flows toward downstream. Thus, the tip of the recirculating flows impinged on the surface of the bluff-body. From this feature, a sharp decrease of $U/U_c$ was observed for $x = 5–7D_o$ (case V) and $x = 10–11.5D_o$ (case IV). Simultaneously, the decreased amount of $U/U_c$ was converted into secondary flow motions due to the conservation of momentum, as shown in the following figure.

Figure 8 presents the area-averaged secondary flow magnitude ($S_{ec}$) along the streamwise direction and its contours of the $x$-$z$ plane at $y/D_o = 0.288$ depending on $L_b$. $S_{ec}$ is defined as $S_{ec} = \sqrt{V^2 + W^2}/U_m$, where $V$ and $W$ are the radial velocity components. $S_{ec}$ for cases IV and V was about 15%–25% versus $U_m$ and its value was sufficiently large to modify the entire flow structure. For case IV, much larger secondary flow motions were observed nearby the bluff-body surface. Due to the increase of vortical motions induced by such azimuthally developed flows, the impinging flows on the bluff-body entrained radially and were mixed with the incoming flow from upstream. This behavior
seemed to be more intensified with the help of strongly developed secondary flows when the bluff-body was inserted further inside the mixing chamber, as in case V. Although secondary flows were also produced near the edge of the bluff-body in cases II and III, the magnitude was too small to induce a noticeable change in the flow structure. The result of the numerical analysis for case III was somewhat dissimilar to that for the experiment, which showed the best performance as regards producing intense and broadened plasma. There were a variety of causes to induce such a discrepancy, where the major reason seemed to be the non-plasma flow conditions. The use of a plasma jet for the inflow condition when conducting further numerical simulations would allow a more extended flow recirculation zone also affecting the bluff-body. Accordingly, further vigorous secondary flow motions and flow mixing to guarantee an intense plasma regime could be ascertained in a similar way to describe the phenomenon for cases IV and V. Therefore, the current numerical results were very meaningful to provide information on the flow structure for predicting plasma-added flow behaviors.

Figure 9 shows the static pressure contours of the x-z plane at y/D₀ = 0.288 and the distribution of the area-averaged static pressure magnitude in the streamwise direction for L₀. As shown, the static pressure on the bluff-body increased when shifting the position of bluff-body upstream.
For cases I–III, the static pressure increased slightly in the flow-developing zone and near the bluff-body. However, cases IV and V showed a definite increase in the static pressure in the vicinity of the bluff-body. This means that the highly convective flows toward downstream were strongly impeded by the bluff-body before they reached a fully developed state. Therefore, the impinging flow appeared with a large amount of static pressure and secondary flow motions. In particular, the mixture near the bluff-body was attributed to the increased static pressure. Thereafter, the newly incoming mixture from upstream impinged again on the remaining previous mixture, resulting in a highly reactive and mixed flow. This feature explains the streamer-like discharge on the surface of the bluff-body in cases IV and V rather than the intense plasma, as shown in Figure 3(c).

B. Optical, electrical, and discharge characteristics

Figures 10(a) and 10(b) show the applied voltages, total currents, and IR emission intensities measured in the nucleation region of the proposed APPJs according to the various positions of the bluff-body. In Figure 10(a), the voltages were relatively high for cases I–III when the bluff-body was spatially away from the plasma region, whereas the voltages decreased in cases IV and V when the bluff-body was closer to the plasma region. In particular, in case V when the bluff-body was in contact with the intense plasma region, the applied voltage was the lowest, meaning that the plasma produced was easily transited into the arc plasma when applying a voltage greater than the one in case V. As shown in Figures 10(a) and 10(b), when compared with cases I and II, the IR emission intensity in case III was increased significantly without any change in the discharge voltage and current. It is worth noting that the optical emission peak shifted to the left, when compared with the case without a bluff-body (case I). However, in cases IV and V, the IR intensities significantly increased even with a lower voltage. These abrupt increases in cases IV and V in Figure 10(b) imply that energetic charged particles flowed into the substrate from the plasma region, inducing severe plasma damage during the plasma polymerization.

Figure 11(a) shows the optical emission spectra (OES) in the wavelength region ranging from 300 to 880 nm measured for the five different cases I–V in the nucleation region of the proposed advanced APPJs. In particular, the detailed optical emission spectra in Figure 11(a) were magnified for the wavelengths ranging from 300 to 420 nm for cases I–III in Figure 11(b) (remote condition), and for cases IV and V in Figure 11(c) (coupling condition). The OES data in Figure 11 show various peaks, such as excited N2, Ar, OH, and carbonaceous (CN) species, existing in the plasma plumes when applying the voltages in Figure 10(a). The various N2 and OH peaks exhibited a higher concentration of reactive nitrogen species (RNS) and reactive oxygen species (ROS), respectively, present in the APPJs with the various positions of the bluff-body; both of these free radicals have been shown to play an important role in various biological/medical and industrial applications and imply the presence of a more efficient, useful, and energy-dense plasma. As shown by the full spectrum measurements in Figure 11(a), various excited nitrogen second positive system (SPS) (N2: 337, 357, and 380 nm) peaks, a carbonaceous (CN; 388 nm) peak, and excited Ar peaks (Ar: 695–850 nm) were significantly increased, especially in case III when the bluff-body was appropriately located inside the guide-tube. The significantly increased Ar peaks (Ar: 695–850 nm) in case III illustrate the excited Ar-rich condition in the nucleation region of the APPJs, which confirms that the monomers could be fully cracked, satisfying the necessary condition for growing plasma polymer thin films, as shown in Figure 11(a). In addition, in Figure 11(b), the strong nitrogen SPS peaks observed in the remote condition of case III were evidence of a plasma energy increase, although no oxygen species peaks were observed. Meanwhile, in Figure 11(c), oxygen species peaks (OH; 308 nm) were observed under the coupling condition of cases IV and V, which may have been
caused by an increase in the local thermal energy induced by the streamer-like discharge ignition presumably due to the location of the substrate closer to the intense plasma plume. Furthermore, the CN (388 nm $\text{B}^2\Sigma \rightarrow \text{X}^2\Sigma$) peak from carbonaceous species, which was emitted during the nucleation processes of the pyrrole monomer, was higher in cases III and IV (Figures 11(b) and 11(c)) with the bluff-body. This means that the presence of carbonaceous species in the proposed APPJs was evidence of sufficient nucleation and fragmentation of the pyrrole monomer.

C. Functionalization and characterization of newly synthesized pPPy nanoparticles using APPJs

Figure 12 shows top and cross-sectional SEM images of the pPPy nanofibers with nanoparticle thin films grown for 30 min on a glass substrate under the five different cases (I–V) of the proposed APPJs. The surface temperature of the substrates during the plasma polymerization under the remote conditions (cases I–III) was about 27, 30, and 30 °C, respectively.63,64 Whereas, under the coupling conditions, with direct contact between the substrate and the intense plasma plume (cases IV and V), the surface temperature of the substrates was about 65 °C and 75 °C, respectively. The morphology and cross-sectional images of the pPPy nanoparticles were characterized by field emission-SEM (FE-SEM, Hitachi SU8220).

In cases I and II, no nanoparticles or amorphous states were observed as the plasmas produced during the nucleation were too weak to crack the monomers efficiently. However, in case III when the bluff-body was appropriately located inside the guide-tube, many nanofibers with nanoparticles were observed to be linked together in uniform and upright networks, meaning that uniform nanofibers and nanoparticles were efficiently synthesized under case III for the proposed APPJs. In general, plasma polymer structures have many irregular cross-linked networks and porous networks. However, the SEM image of case III in Figure 12 confirmed polymer structures with regular networks, not irregular cross-linked networks. It was noticeable that the height and density of the pPPy nanofibers/nanoparticles were significantly increased by the advanced APPJ technique at a low temperature. Whereas, in cases IV and V, many nanofibers and nanoparticles were observed to be damaged and melted down, which was induced by the severe ion bombardment and thermal damage due to the strong streamer discharge. In addition, as shown in Figure 12, the deposition rate in case III was increased significantly at about 0.93 μm min⁻¹ under the low-temperature process, meaning that the nano-size...
polymer grew rapidly during the plasma polymerization in the proposed APPJs without a thermal solution process.

Figure 13 shows the transmission electron microscopy (TEM) images of the pPPy nanoparticles prepared under case III of the proposed APPJs. The high-resolution TEM (HR-TEM) images and fast Fourier transform selected area electron diffraction (FFT-SAED) patterns were taken with a Titan G2 ChemiSTEM Cs Probe (FEI Company, Hillsboro, Oregon, USA) transmission electron microscope, operating at 200 kV. The TEM samples were prepared by

FIG. 12. Top and cross-section views of scanning electron microscopy (SEM) images of the plasma-polymerized pyrrole (pPPy) nanoparticle thin film prepared via APPJs after 30-min deposition relative to various positions of bluff body (cases I–V). Scale bar = 2 μm.
depositing a 6 μl solution of pPPy nanofibers with nanoparticles (ultrasonically dispersed in DI water) on carbon-coated copper grids, and dried in air. As shown in Figures 13(a) and 13(b), pPPy nanoparticles with a diameter range of 5–25 nm were clearly observed. The FFT-SAED pattern of pPPy nanoparticles (Figures 13(a) and 13(b), insets) revealed single- and poly-crystalline characteristics. In particular, the FFT-SAED pattern of pPPy nanoparticles (Figure 13(a), inset) revealed a clear diffraction spot of a single-crystalline characteristic. From an atomic point of view, conventional polymers and plasma-based polymers are composed of many conjugated bonds without a constant direction. However, the polymer that was polymerized using the proposed APPJs with a bluff-body exhibited a single-crystalline characteristic with a constant direction of atoms. As shown by the TEM images in Figure 13, the directional arrangement of the polymer atoms was likely caused by ion and electron-charged particles with a constant directionality in the intense and broadened plasma, resulting in a single-crystalline characteristic for the pPPy nanoparticles. Furthermore, from a molecular point of view, the single-crystalline characteristic of the pPPy nanoparticles may also have been caused by the regular-uniform and upright networks, as shown by the SEM image in Figure 12 (case III). Investigations of these detailed mechanisms will be reported in future work. Therefore, the current experimental results revealed that single-crystalline high-density plasma-polymerized pyrrole (pPPy) nanoparticles were successfully synthesized at a low temperature when using the advanced atmospheric pressure plasma polymerization technique. The nano-structures of the resulting pPPy were visualized using energy dispersive x-ray spectroscopy (EDS) elemental mapping and high-angle annular dark-field scanning TEM (HAADF-STEM), as shown in Figures 13(c) and 13(d). Plus, the EDS and elemental mapping results revealed that the pPPy nanoparticles were exclusively composed of C, O, and N. Consequently, the TEM analysis of Figure 13 indicated that the plasma polymerization using the proposed APPJs in case III generated uniform pPPy nanoparticles of small size with a single-crystalline characteristic.

Figure 14 shows the Fourier transform infrared spectroscopy (FTIR) spectra of the pPPy nanofibers and nanoparticle thin film synthesized on the plastic substrates with the five different cases (cases I–V in Figure 2(a)) using the advanced APPJ technique. For all five cases, the deposition time was identical, i.e., 60 min, with a low process temperature. The FTIR spectra of these polymers films were measured using a Perkin-Elmer Frontier spectrometer between 650 and 4000 cm⁻¹. As shown in Figure 14, the FTIR spectra were determined using a transmittance method since the pPPy films grown in this experiment were too thin to use an absorbance method. In cases III–V, the characteristic peaks of pPPy were measured at 3285 cm⁻¹ (N-H stretching with hydrogen bonded 2° amino groups) and 2960 cm⁻¹ (aliphatic C–H stretching absorption). Plus, a –C¼H aliphatic vibration...
peak was observed at 2215 cm\(^{-1}\). These peaks implied that some of the pyrrole rings in the polymer were fragmented.\(^{28,31,71}\) Furthermore, different absorptions corresponding to alkenes that reflected broken rings showed peaks at 805 cm\(^{-1}\) and 730 cm\(^{-1}\), plus there was a C–C double bond peak at 1690 cm\(^{-1}\). These peak regions were evidence of films with a better electric conductivity,\(^{28,31,72}\) while also indicating the successful formation of pPPy. Consequently, these experimental results confirmed that proper control of the process parameters with the proposed APPJ device, that is, case III, enabled the growth of high-density ultra-fast pPPy thin films and nanoparticles at a low temperature. It is also expected that the proposed device can be used for plasma polymerization with various monomers. Moreover, from a treatment and etching point of view, cases IV and V can be beneficial due to direct contact of the substrate with an intense plasma plume and strong streamer-like plasma. Therefore, to reveal the plasma mechanism of the proposed APPJs for large-area treatment, several options (e.g., the number of jet arrays, bluff-body size) will be explored in future studies.

**IV. CONCLUSIONS**

This paper investigated the use of a glass guide-tube and polytetrafluoroethylene (PTFE) bluff-body as a main part of the advanced atmospheric pressure plasma source for the low-temperature synthesis of single-crystalline high density plasma-polymerized pyrrole (pPPy) nano-materials, based on parametric studies of the intense and broadened atmospheric pressure plasma jets (APPJs). Three process parameters, including the position of the bluff-body, Ar gas flow rate, and remoteness of the substrate from the intense and broadened plasma, were varied and the experimental and numerical results confirmed that intense and broadened plasma showing a glow-like discharge characteristic was produced in a large area when properly adjusting the Ar gas flow rate and position of the bluff-body with respect to the guide-tube. In particular, the appropriate location of the bluff-body with respect to the guide-tube under specific Ar gas flow rates enabled full cracking of the monomers in the nucleation region due to a longer sustainment of the Ar species. Furthermore, positioning the substrate away from the intense and broadened plasma (i.e., remote condition) facilitated successful low-temperature synthesis of single- and poly-crystalline pPPy nanoparticles with a size of a few tens of nanometers, due to the suppression of etching and thermal damage on the glass or plastic substrate during the plasma polymerization. Thus, by properly adjusting the three process parameters, single-crystalline pPPy nanoparticles linked together in uniform and upright networks were obtained when using the proposed APPJ device, as confirmed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). It is also expected that the growth of pPPy nanoparticles with a single-crystalline property using a low-temperature process will provide a unique advantage for many applications, such as molecular electronics, opto-electronics, and nanodrug/gene delivery in nanomedicine.

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**References**
