Brush-Paintable Black Electrodes for Poly(vinylidene fluoride)-Based Flexible Piezoelectric Devices

Sang-Hwi Lim, Hyeong-Min Sim, Gyewon Kim, and Han-Ki Kim*

ABSTRACT: We investigated simple and unrestricted brush-paintable black electrodes for poly(vinylidene fluoride) (PVDF)-based artistic flexible piezoelectric devices. The conductive black ink for paintable electrodes was synthesized by mixing poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and typical black ink and optimizing the mixing ratio. At an optimal mixing ratio, the brush-paintable black electrodes showed a sheet resistance of 151 Ω/sq and high coatability for flexible piezoelectric devices. Noticeably, higher black ink ratios increased adhesion forces, while diminished the shear flow of the conductive black ink. In addition, the optimized conductive black electrode exhibited an outstanding level of mechanical flexibility due to good adhesion between the black electrode and the PVDF substrate. During the repeated inner/outer bending fatigue tests with high strain, no resistance change confirmed the outstanding flexibility of the brush-paintable conductive electrode. As a promising application of the brush-paintable optimized black electrode, we suggested highly flexible piezoelectric devices that can be used. A PVDF-based piezoelectric speaker and a generator with the brush-paintable black electrode showed acoustic and output signal values approximate to those of metallic electrodes fabricated by vacuum-based high-cost thermal evaporators. Our experiment demonstrated a cost-efficient and simple process for fabricating brush-paintable electrodes, applicable to the flexible PVDF-based piezoelectric devices.

1. INTRODUCTION

Recently, the rapid development of lightweight, low-cost acoustic, and energy-harvesting devices with high mechanical flexibility and easy fabrication has been promoted for the application to wearable electronics for the human body.1–6 More attention has been paid to the development of high-quality flexible electrodes with low cost to realize wearable electronics. In this regard, there has been a particular focus on developing brush-paintable artificial electrodes applicable to current wearable electronic devices. To date, electrodes for the flexible wearable devices have been fabricated by an expensive vacuum-based process by using metals (Ag and Cu) or metal oxides (InSnO).7–10 However, the high material cost and poor flexibility of ITO electrodes limit their application as a next-generation technology for flexible electrodes.11–16 Researchers have conducted extensive investigations to find a replacement for ITO electrodes that shows better flexibility, such as oxide,17 metal/oxide multilayer (OMO),18–20 metal nanowire,21 carbon nanotube,22,23 graphene,24,25 and conductive polymers.26–28 Among these candidates for next-generation technology for flexible electrodes, poly(3,4-ethyylene dioxythiophene):poly(4-styrene sulfonate) (PEDOT:PSS),29–31 has been applied to the electrodes made for various flexible devices, such as flexible thin-film speakers and energy generators.32–35 photodiodes, photosensors,36,37 electrochromic windows,38,39 field-effect transistors,40 and solar cell materials.41–43 Among these, flexible piezoelectric devices have been considered an important application because their mechanical flexibility, endurance, and performance can meet the qualification for flexible electrodes.

For flexible, acoustic, and energy-harvesting devices, β-phase poly(vinylidene fluoride) (β-PVDF) piezoelectric films have been widely employed because of their excellent piezoelectric properties and advantages such as high piezoelectric constant with high dielectric strength, superb mechanical properties, wide frequency range response, and low acoustic impedance.44–49 Although PEDOT:PSS and PVDF have been widely used as electrodes and active layers for piezoelectric devices, there has been no research on brush-paintable electrodes applicable to PVDF-based piezoelectric devices.

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Furthermore, it has not been investigated yet how to enhance the spreadability and connectivity of brush-painted PEDOT:PSS on a PVDF substrate. Especially, other solution processes such as spin coating, doctor blade coating, inkjet printing, and spray coating have disadvantages, for example, wastage of solution, limitation of design and patterning, and nozzle clogging. However, brush painting has advantages including simplicity, cost efficiency, ambient atmosphere processing, and electrodes can be painted with no limits to design, type of solution, or substrate. Thus, it is imperative to research brush painting of PEDOT:PSS onto PVDF piezoelectric film to achieve the cost efficiency of PVDF-based flexible piezoelectric devices.

In this work, we report on the characteristics of a brush-paintable conductive black electrode (CBE) coated using a hybrid ink of PEDOT:PSS mixed with charcoal-based black ink on a PVDF-based piezoelectric substrate. To determine the optimal mixing ratio, we investigated the properties of brush-paintable CBEs as a function of the mixing volume ratio. We also compared the performance of PVDF-based piezoelectric devices fabricated with the low-cost CBE with that of devices that used a high-cost WO3−PVDF substrate.

### 2. EXPERIMENTAL DETAILS

#### 2.1. Synthesizing Conductive Black Ink

Conductive black ink was synthesized by mixing water-based PEDOT:PSS with high conductivity (Clevios PH1000, Heraeus) with charcoal-based black ink, commonly called meok in Korea. Meok has good coatability because it includes adhesive properties such as animal glue and carbon particles. Therefore, the low coatability of PEDOT:PSS on a hydrophobic PVDF substrate can be improved by adding black Korean ink. To optimize the mixing ratio, mixtures of PEDOT:PSS and black ink with mixing volume ratios of 1:0, 20:1, 10:1, 5:1 were fabricated. Then, the mixtures were sonicated in a sonication bath for 10 min, in which, as shown in Figure 1a, a well-dispersed solution was produced.

#### 2.2. Brush Painting of Conductive Black Ink on the PVDF Film

The CBEs were directly painted onto the ozone-treated β-PVDF substrate with a 1.5 cm wide paintbrush, which is made of nylon fibril, as shown in Figure 1b. After the CBEs were painted on the β-PVDF substrate, the samples were dried at 70 °C for 10 min using a hot plate. Made of usual Korean meok and PEDOT:PSS, the CBE could be easily used and freely painted in any circumstances; therefore, the CBE on the β-PVDF substrate could function in multiple ways ranging from sound technology to visual arts and interior design to the energy industry.

#### 2.3. Deposition of the WO3−Ag/WO3−x (WAW) Multilayer Electrode

The bottom WO3−x layer, middle Ag layer, and top WO3−x layer were evaporated on a β-PVDF substrate continuously without breaking the vacuum using a thermal evaporation system (15NNS005, NNS Vacuum). The base pressure of the evaporation process was under 1 × 10−6 torr and the rotation speed was 11 rpm. The thicknesses of each WO3−x layer and Ag layer were 30 nm with a deposition rate of 0.25 nm/s and 12 nm with a deposition rate of 1.00 nm/s, respectively.

#### 2.4. Fabricating a Piezoelectric Speaker and a Nanogenerator

The optimized CBE was painted on the front of the β-PVDF substrate as a front electrode and the WAW multilayer electrode was thermally evaporated on the rear of the β-PVDF substrate as a rear electrode to make a CBE-applied piezoelectric speaker and a generator. As a comparison target, reference piezoelectric devices with the WAW electrode deposited on both sides of the β-PVDF substrate were fabricated. The flexible WAW multilayer film has low resistivity (3.77 Ω-cm) and high transmittance (92.16%) as previously reported. For contact electrodes, we coated Ag paste on the edge of the front and rear electrodes on both sides of the β-PVDF substrate and attached Cu tape on the edge electrode; to ensure a good-quality CBE for the piezoelectric devices, we repeatedly painted and dried out the fabricated ink a total of six times, as illustrated in Figure 1b.

#### 2.5. Electrodes and Devices Characterizations

The electrical properties of the CBE were measured with a four-point probe (FPP-HSS, DASOL ENG), and the spreadability of the brush-painted CBE was analyzed with a CMOS sensor-based spreadability measurement system. The surface morphology of the CBE on the β-PVDF substrate was examined using a field emission scanning electron microscope (FESEM: JSM-7600F, JEOL), measuring the CBE surface contact angles on the substrate with different mixing ratios using a contact angle measurement system (Phoenix-MT(A),...
Figure 2. (a) Contact angle change of the CBE with different PEDOT:PSS and black ink mixing volume ratios (1:0, 20:1, 10:1, and 5:1) on the untreated and UV-ozone-treated PVDF substrates as a function of time. (b) Spreadability of brush-painted CBEs on the PVDF substrate by the number of brush strokes.

Figure 2a clarifies, 10 min of UV-ozone treatment drastically decreased the contact angles of PEDOT:PSS and all CBE sessile droplets on the PVDF surface. However, the contact angles of the droplets on the treated PVDF had no relevance to the mixing volume ratio (Figure S2b). Figure 2b shows the spreadability of the brush-painted CBE on the UV-ozone-treated PVDF substrate with respect to the number of brush strokes and mixing volume ratios; we calculated the spreadability of solutions using the following equations with histogram analysis data based on the photographs of the samples captured by the CMOS camera (Figure S3)

\[
\text{Spreadability} = \begin{cases} 
\frac{(255 - \text{SD}) \times 100\%}{255} & \text{for } M \geq \frac{255}{2} \\
\frac{\text{SD} \times 100\%}{255} & \text{for } M < \frac{255}{2} 
\end{cases}
\]

where SD and M are, respectively, the standard deviation and mean color intensity (from 0 to 255), attained from histogram analysis, of each pixel of the sample images. When M was lower than 127.5, which is the median of the color intensity range, the measured sample was a relatively bright color because the uncoated area of the CBE was larger than the coated area; in contrast, when M exceeded 127.5, the measured sample was relatively dark because the CBE’s coated area was larger than the uncoated area. In this case, a smaller SD indicated that the deviation of the color intensity was smaller because the CBE had a more uniformly coated on the PVDF substrate; this feature indicated that a given sample had achieved better coatability with higher spreadability. On the contrary, the large SD value means a large color intensity deviation caused by the bad uniformity of the brush-painted electrode, which reflects poor coatability with the low spreadability of ink. As the number of CBE brush strokes and the mixing volume ratio increased, the spreadability of the solution also increased. However, despite the enhanced wettability of PEDOT:PSS and CBE on the surface-treated PVDF substrate, as shown in Figure S2b, there was relatively little improvement of the PEDOT:PSS spreadability with an increasing number of brush strokes. In contrast, when the black ink was in high concentration, the spreadability of the CBEs was enhanced more, even under the same experiment condition. Also, its spreadability rapidly enhanced, when the number of brush strokes increased. In the PEDOT:PSS-only sample, we observed that the applied shear stress from the paintbrush.

3. RESULTS AND DISCUSSION

Figures 2a and S2 show the contact angles that drop from the different hybrid conductive black inks on the untreated and UV-ozone-treated PVDF substrates in the process of time. The CBEs we used to measure the contact angles comprised PEDOT:PSS and black ink mixed at the ratios of 20:0, 20:1, 20:2, and 20:4. Before the UV-ozone treatment of the PVDF substrate, all sample contact angles over time were almost identical to the initial contact angle, regardless of the mixing volume ratios, as shown in Figure 2a; however, as the volume ratio of black ink increased, the initial contact angle decreased, as shown in Figure S2a. In particular, a sessile droplet of PEDOT:PSS only showed a similar contact angle with the water, owing to the high water content of the water-based PEDOT:PSS solution; furthermore, the wettability of the CBE slightly increased too, along with the increasing ink volume ratios. However, when the black ink mixing volume exceeded 10% of PEDOT:PSS, we observed no clear changes in the CBE contact angle by mixing volume or time. In addition, the contact angles tended to clearly converge near 76° as time passed, due to the hydrophobic surface of PVDF. These results indicate that chemical bonding and reactions occurred at the interfaces of the PVDF surface and the CBE solution and rarely changed with the increasing black ink volume ratios; however, a contact angle over 76° is too high to make a stable adhesion between the CBE and the PVDF substrate. Therefore, to improve the wettability of the CBE, we studied the effect of the UV-ozone treatment on the PVDF surface. As the number of brush strokes increased, the spreadability of the CBE rapidly enhanced, when the number of brush strokes increased. In the PEDOT:PSS-only sample, we observed that the applied shear stress from the paintbrush.

SEO Co.). The flexibility of the CBE coated on the β-PVDF substrate was investigated using a means of a lab-designed inner/outer bending test system. The acoustic properties were investigated using an audio analyzer (SR1, Stanford Research Systems) in an anechoic chamber. During the test, a DC source was supplied by a lab-designed amplifier with a power supply unit (OPS 3010, ODA Technologies) to the PVDF piezoelectric speaker through a Cu contact electrode. The generated voltage of the PVDF-based piezoelectric nanogenerators (PENGs) was measured with a digital oscilloscope (DPO 3052, Tektronix) connected with an input impedance of 40 MΩ to measure in an open circuit; the output current under short-circuit conditions was also measured using a low noise current amplifier (DLPCA-200, FEMTO). To generate a piezoelectric signal, repeating strains on the devices were applied with a bending machine (Junil-Tech).
caused delamination in some regions during the repetition of brush painting. Noticeably, when the mixing volume ratio was 10% or higher, and the number of brush strokes exceeded three, the spreadability of the solutions achieved near saturation. This indicated that when multiple brush strokes brought about a uniform CBE coating, the mixing volume ratios for the uniform coating did not need to exceed 10% of PEDOT:PSS. From these results, we concluded that the amount of the adhesive component in the CBE at a 10:1 mixing volume ratio provided a sufficient adhesion for coating the PVDF substrate. In this regard, it was clear that the adhesive ingredients in the black ink caused the enhancement of the coatability of the solution itself, as illustrated in the better coatability obtained from the high concentration of black ink. Furthermore, it was clear that the better spreadability of the CBE, enabled by the high concentration of black ink, had no correlation with the wettability, given that the contact angle differences between PEDOT:PSS and CBE were sufficiently small to be considered measurement errors.

Figure 3a shows the average thickness and standard deviation of the six-times-painted CBE at different mixing volume ratios. Figure 3b shows the dynamics of the brush painting on the PVDF substrate. As easily extrapolated from an initial assumption and a previous analysis result that the adhesive components of the black ink caused the enhancement of the coatability of the solution itself, the CBE became thicker as the mixing volume ratio increased. Because of the capillary effect caused by the porosity of the paintbrush bristles and the poor wettability of the DI water solvent of PEDOT:PSS, PEDOT:PSS itself is difficult to coat on the hydrophobic surface of PVDF. However, as the mixing volume ratio of black ink increased, the capillary effect and paintbrush shearing force decreased because the cohesive force of the solution increased due to the increasing adhesive components. As a result, the brush-painted CBE tends to stay in its initial position on the PVDF substrate rather than flowing along with the brush, and this led to the smaller shear flow of the solution and thicker film coating. Moreover, the enhanced coatability and decreased delamination enabled by the reduction of brush shear stress led to an increasing spreadability, as shown in Figures 2b and S3. In particular, the thickness of the brush-painted electrode with PEDOT:PSS was less than 1/3 that of the other CBE, with a larger standard deviation in the thickness because of its poor spreadability; this fact indicated that the CBE thickness and coatability were greatly affected by the shear flow changes according to the different mixing volume ratios. Figure 3c shows the average sheet resistance measured by the four-point probe and standard deviation of the CBE on the PVDF substrate according to different PEDOT:PSS and black ink mixing ratios and different numbers of brush strokes. As the number of brush strokes and the mixing volume ratios increased, the sheet resistance of the CBE decreased due to its increased thickness and enhanced coating uniformity. In particular, when the CBE was brush-painted onto the substrate six times, the CBES at the ratios of 10:1 and 5:1 exhibited the sheet resistances of 171.9 and 150.9 Ω/sq, respectively. To find the optimum mixing volume ratio, we calculated the conductivity of the CBE based on the following equation

\[
\sigma = 1/\rho = R_{\text{sheet}} \times t
\]

where \(\sigma\) and \(\rho\) are the calculated conductivity and resistivity of CBE, respectively, and \(R_{\text{sheet}}\) and \(t\) are the sheet resistance and thickness of the six-times-brush-painted CBE, respectively.
As summarized in Table 1, with increasing mixing volume concentration, the CBE conductivity increased until the ratio with respect to PEDOT:PSS reached 0.1 and showed 25.7 S cm⁻¹; however, when the mixing volume ratio exceeded 0.1, the conductivity decreased as the mixing volume ratio increased. This can be interpreted as reflecting a trade-off that occurred with increased mixing volume ratio: as the ratio increased, the connectivity of the CBE increased with enhanced spreadability, but the electrical conductivity decreased with the increased concentration of black ink. This is due to the fact that the black ink, mixed within the CBE, was an essential impurity in the conductor, although it acts as an adhesive and percolation conduction enhancer. Given this feature, this trade-off is significant in the process of fabricating and optimizing the CBE. In particular, a mixing volume ratio of 0.1 was suitable for improving the connectivity, minimizing the resistivity caused by impurities, and obtaining the best electrical properties of the CBE. Figures 3d and S4 demonstrate that the optimized CBEs brush-painted onto the PVDF substrate had sufficient conductivity to act as interconnectors for lighting commercial LEDs with DC power applied to the interconnector.

Figure 4a,b shows FESEM images obtained from six-times-brush-painted PEDOT:PSS in a single layer and the optimized CBE on the PVDF substrate, respectively. As the images show, the PEDOT:PSS electrode has a relatively flat surface compared with the CBE; the CBE has a porous and rougher surface morphology with the agglomeration of the PEDOT:PSS and carbon nanoparticles. In the CBE ink, the adhesive enhanced the cohesive force of the solution, and the carbon nanoparticles acted as the nuclei of the agglomeration. In this way, PEDOT:PSS suspended in the CBE ink prefers to adhere to the carbon nanoparticles and easily creates large aggregates that cause great surface roughness (inset image of Figure 4b). Furthermore, this phenomenon of aggregations clearly demonstrates the function of the black ink as a cohesive enhancer in the CBE solution and therefore it substantiates our previous analysis of the CBE. Although the single-layer brush-painted PEDOT:PSS exhibited better surface roughness at the microscopic scale, it showed inferior electrical properties and was inhomogeneous in addition to its extreme roughness at the macroscopic scale because of the low spreadability of the solution on the PVDF substrate when painted with a brush.

To demonstrate the mechanical flexibility of the brush-painted CBE coated on the PVDF film, we performed inner and outer bending tests as shown in Figure 5a; the inset of the figure schematically illustrates the definition of inner and outer bending tests and applied forces on the CBE. In the inner bending test, the brush-painted CBE bent concavely and experienced compressive stress; in the outer bending test, the brush-painted CBE was curved convexly and experienced tensile stress. In both cases, maximum stresses are applied in the center of the film. As such, any mechanical deformation in the CBE on the PVDF substrate such as cracks, physical separation, or delamination will lead to changes in the measured resistance. Therefore, by monitoring resistance changes of the brush-painted CBE along with a decreasing bending radius, we could evaluate the mechanical flexibility of the CBE on the PVDF film, based on the changes in resistance ($R_{\text{change}}$) that the following equation defines

$$R_{\text{change}} = \frac{|R - R_0|}{R_0}$$  \hspace{1cm} \text{(3)}$$

where $R$ and $R_0$ are the measured resistance with respect to the bending radius and initial resistance of the sample, respectively; we then calculated $R_{\text{change}}$ based on these values and plotted according to the bending radius, as shown in Figure 5a. Regardless of the bending radius and bending test conditions, the optimized CBE showed a constant resistance change within 5% of the margin of error, and this fact indicated excellent mechanical flexibility of the brush-painted CBE on the PVDF substrate. In particular, even at a small bending radius of 1.0 mm in both inner and outer bending modes, there was no abrupt increase of $R_{\text{change}}$. We calculated the peak strains applied to the CBE with the following equation

$$\text{Strain} = \frac{d_{\text{CRE}} + d_{\text{PVDF}}}{2R} \times 100\%$$  \hspace{1cm} \text{(4)}$$

where $R$ is bending radius and $d_{\text{CRE}}$ and $d_{\text{PVDF}}$ are the thickness of the CBE (2.3 μm) and the PVDF substrate (85 μm), respectively. Both outer and inner bendings at 1.0 mm radius

| Table 1. Thickness and Electrical Properties of Brush-Painted CBEs at Different Mixing Volume Ratios of PEDOT:PSS and Black Ink (Meok) |
|--------------------------------------------------|
| volume ratio of PEDOT:PSS/black ink | thickness [μm] | sheet resistance [Ω/sq] | conductivity [S/cm] |
|---------------------------------------|----------------|------------------------|-------------------|
| 1/0                                   | 0.656          | 3377                   | 4.51              |
| 20/1                                  | 1.97           | 367.3                  | 13.8              |
| 10/1                                  | 2.27           | 171.9                  | 25.7              |
| 5/1                                   | 3.20           | 150.9                  | 20.7              |

Figure 4. (a) Surface FESEM image of a brush-painted PEDOT:PSS electrode. (b) CBE with a PEDOT:PSS to black ink volume ratio of 10:1. Insets are magnified surface FESEM images.
generated a maximum level of tensile and compressive strain of 4.4% to the CBEs, respectively. The outstanding flexibility of the CBE-applied film appears to have been achieved by the flexible PEDOT:PSS-based CBE and the PVDF substrate, and good adhesion between these as noted earlier. Furthermore, we conducted dynamic bending fatigue tests at a constant bending radius of 2.0 mm in inner and outer bending modes 10 000 times, as shown in Figure 5b. During repeated inner/outer bending tests with high applied compressive/tensile stress, we observed no resistance change in either bending mode because of the CBE’s better tolerance to mechanical flexibility. Figure 5c,d presents the FESEM images of the CBE on the PVDF substrate before and after (c) inner and (d) outer fatigue bending tests.

Figure 5. (a) Inner and outer bending tests of the brush-painted CBE on the PVDF substrate with the bending radius decreasing from 25 to 1 mm. The inset shows the bent sample experiencing compressive and tensile stress applied to the CBE. (b) Resistance changes during 10 000 cycles of inner and outer bending of the brush-painted CBE. The inset shows dynamic bending steps. The surface FESEM image of the CBE on the PVDF substrate before and after (c) inner and (d) outer fatigue bending tests.

Figure 6. (a) Schematic diagram showing an CBE/PVDF/WAW piezoelectric speaker structure and working principle. (b) Photograph of the brush-painted CBE applied in the piezoelectric speaker performance test setup. (c) Frequency response of the sound pressure level (SPL) and (d) total harmonic distortion (THD) of the PVDF-based piezoelectric speaker with different front electrodes (OMO as control, CBE as experimental).
research showed that the PVDF-based piezoelectric speaker between the SPL response of the piezoelectric speakers with painted CBE was 100.5 ± 4.1 dB; moreover, the difference between the SPL response of the piezoelectric speaker at 10 cm and conducted the measurements within the anechoic chamber to minimize the interference of the baseline noise.

Because of the differences in electronegativity between the fluorine and hydrogen atoms, the fluorine-oriented side of the β-PVDF is negatively charged, while the hydrogen-oriented side has a positive charge. As a result, β-PVDF had piezoelectric properties, and the PVDF sheet contracted when the applied external electric field was aligned in the opposite direction from the PVDF pole direction; the sheet stretched when the applied external electric field was aligned along with the pole direction of the PVDF, as illustrated in Figure 6a. Therefore, we could control the vibration of the PVDF-based piezoelectric speaker and generate sound by modulating the applied voltage on both sides of the electrodes. Furthermore, to generate better-quality sounds, the electrodes should be highly conductive to form a strong and uniform electric field along the whole area of the PVDF sheet. In addition, electrodes should be highly flexible for the smooth vibration of the PVDF-based piezoelectric speaker. Figure 6b is a photograph that shows the frequency response experiment setup for a flexible PVDF-based piezoelectric speaker with a brush-painted CBE. For the measurements, we fixed the distance between the microphone and the PVDF-based piezoelectric speaker at 10 cm and conducted the measurements within the anechoic chamber to minimize the influence of the baseline noise.

Table 2. Acoustic Properties (Frequency Response of the SPL and THD) of a Fabricated PVDF-Based Piezoelectric Speaker with Different Front Electrodes (OMO: Control, CBE: Experimental)

| acoustic properties (frequency range) | front electrode of the PVDF-based piezoelectric speaker |
|--------------------------------------|-------------------------------------------------------|
|                                      | WAW (control)                                         |
| average SPL (20 Hz−20 kHz)           | 81.6 ± 20.1 dB                                        |
| average THD (20 Hz−20 kHz)           | 6.6 ± 11.2%                                           |
| average SPL (1 kHz−10 kHz)           | 101.0 ± 3.9 dB                                        |
| average THD (1 kHz−10 kHz)           | 8.4 ± 12.5%                                           |
| average SPL (20 Hz−20 kHz)           | 81.7 ± 19.2 dB                                        |
| average THD (20 Hz−20 kHz)           | 9.6 ± 11.9%                                           |
| average SPL (1 kHz−10 kHz)           | 100.5 ± 4.1 dB                                        |
| average THD (1 kHz−10 kHz)           | 8.1 ± 12.1%                                           |

where \( A_i \) and \( A_1 \) are the power level of \( i \)th harmonic and the fundamental tone, respectively. As Figure 6d and Table 2 show, in the frequency range of 1−10 kHz, the average THD of the fabricated PVDF-based piezoelectric speakers was less than 10%. In particular, the distributions of the THD response of the PVDF-based piezoelectric speakers with the front WAW electrode and the front CBE were 8.4 ± 12.5 and 8.1 ± 12.1%, respectively. Considering these acoustic properties of PVDF-based piezoelectric speakers, the brush-painted CBE was adequate as the electrode in the piezoelectric devices, owing to its superior flexibility and moderate electrical properties.

Table 2 shows the structure of a brush-painted CBE-based piezoelectric generator and the configuration of the test system. To increase harvest efficiency with enhanced piezoelectric properties, we conducted the electrical poling in advance of taking the measurements to align the dipoles parallel with the applied electric field of the piezoelectric PVDF. We measured the output signals of PENGs with an oscilloscope during the repeated cycle of bending and releasing, and we measured the output voltage and current graph with respect to time in open and short-circuit conditions, respectively. Figure 7b shows the cyclic changes, in terms of the output voltage produced by the bending and releasing cycle of PENGs with different front electrode materials (WAW: bold line, CBE: thin line). During the cycle, compressive and tensile stress were applied on the PVDF layer and corresponded with output voltage peaks with a different sign. When the PENG was released (first stage) by the bending machine from the bent state (initial state), applied compressive strain was released from the PVDF layer. The piezoelectric potential changed to the opposite direction by the restored polarization in the poling direction. As a result of this process, electrons flowed out in the poling direction for charge compensation and appeared as a corresponding positive voltage peak. In contrast, when the PENG was curved (second stage) by the bending machine, compressive stress applied on the PVDF layer built up the piezoelectric potential difference across the sheet by...
decreased polarization in the poling direction. As a result of this, electrons flowed in the opposite direction of the poling direction for charge compensation and appeared as a corresponding negative voltage peak, returning to the equilibrium state when the full cycle was complete. Notably, the output voltage response of the PENG with the WAW front electrode according to the applied force was faster than the CBE front electrode. Moreover, the PENG with the WAW front electrode exhibited narrower, discrete voltage peaks, while the PENG with the front CBE was slower and showed broad, blunt voltage peaks. These results seem to originate from the different sheet resistance of the WAW (3.77 Ω/sq) and CBE (171.9 Ω/sq). In particular, owing to the high sheet resistance, great surface roughness, and many defects created with black ink that could act as trap sites, poling of the brush-painted CBE was not effectively conducted, and the degree of the poling of the PENG with the rough CBE was lower than that for the PENG with the flat WAW electrode with very low sheet resistance. Moreover, because of the higher resistance of the CBE, it was more difficult for the generated charge to flow out to the wire than the WAW electrode-based PENG does. These facts explain the slower and broader response signal of the PENG with the front CBE, compared with that with the front WAW electrode. As shown in Figure 7c,d, we observed the same tendency in the repeated cycles of the open-circuit voltages and short-circuit currents of the PENGs during the repetitive mechanical deformations. Although the CBE-applied PENG exhibited slower piezoelectric properties than those of the WAW-applied generator, the signal values were comparable with the same order of magnitude. These facts demonstrate the critical potentials of brush-painted CBEs as highly flexible, mechanical, and endurable thin-film electrodes applicable to the different types of flexible PVDF-based piezoelectric devices including a speaker and a generator.

4. CONCLUSIONS

We investigated a flexible CBE fabricated by simple and unrestricted brush paintings, which can be used for PVDF-based flexible piezoelectric devices. We also assessed the performance of the brush-painted flexible CBE in the fabricated devices. The CBE is a hybrid electrode formed by synthesizing highly flexible PEDOT:PSS and traditional Korean black ink that was designed and optimized to enhance coatability and electrical properties. The optimized CBE achieved good coatability on the PVDF substrate, since it diminished the shear flow of the CBE during the process of brush paintings, and the fabricated electrode showed a low sheet resistance of 151 Ω/sq with outstanding flexibility. In short, the fabricated PVDF-based flexible piezoelectric speaker and generator with the optimized CBE showed superior performability comparable to that of a speaker and a generator with a WAW electrode. In particular, in the frequency range from 1 to 10 kHz, the PVDF-based piezoelectric speaker exhibited mean SPL and THD over 100 dB and less than 10%, respectively, which are similar to the values for highly conductive WAW electrode-applied devices. Moreover, as illustrated in the case of the PVDF-based PENG, although the brush-painted CBE generator showed slower and blunter piezoelectric properties than the WAW-applied generator, output values of the former were similar to the latter. We demonstrated that a highly flexible brush-painted CBE was a...
prospective candidate to replace conventional low-flexibility electrodes in PVDF-based piezoelectric devices. Furthermore, the brush-painting approach was simple, cost-efficient, unrestricted, and user-friendly, and because of this, the brush-paintable electrodes could meet the diverse technological demands that need a higher level of flexibility and adjustability, such as PVDF-based flexible piezoelectric devices.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04369.

Process of drawing a CBE on the PVDF substrate to fabricate a piezoelectric speaker (Figure S1); contact angles of the CBE and the PEDOT:PSS solution on the PVDF substrate according to the time before surface treatment and after UV/ozone treatment of the PVDF surface (Figure S2); photography and histogram analysis data show the spreadability of the brush-painted CBE on the UV-ozone-treated PVDF substrate with respect to the number of brush painting strokes and concentration of the Sumi ink (Figure S3); resistor symbol-shaped CBE drawn on the PVDF substrate as a flexible circuit between the battery and LEDs; and flexibility of the brush-painted CBE enabled turning on the LED under various bending conditions (Figure S4) (PDF)

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