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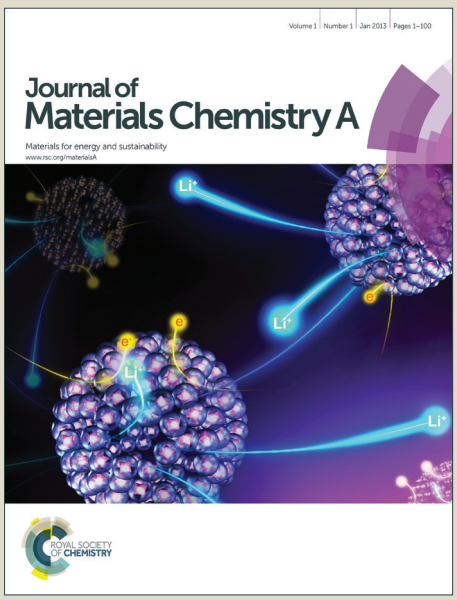

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PAPER

Highly conductive PEDOT electrodes for harvesting dynamic energy through piezoelectric conversion

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A highly conductive PEDOT was explored as a transparent electrode for a piezoelectric PVDF film. The potential of a piezoelectric film device consisting of PEDOT/PVDF/PEDOT layer was realized in fabricating a transparent and flexible energy harvester that generates electricity from repetitive physical displacements (stretching and pressing). The output voltage and current density of the energy generator were 16.4 V (peak-to-peak) and 0.2 μA cm^{-2} (peak-to-peak), respectively, when applying 800 mN of stretching power. These values are much higher than the PEDOT:PSS-CNT system and comparable to those reported earlier for inorganic-based nanogenerators. Finally, a self-lighting system consisting of an LED bulb, capacitor, and the PEDOT/PVDF/PEDOT device was demonstrated under a dynamic stretching condition, allowing for large-scale, low-cost production of a miniaturized active thin-film energy harvester.

Introduction

With energy needs for low-power mobile and biomedical applications rapidly increasing, harvesting physical energy from humans is a crucial technology for extended and reliable operation.[1-5] Thermoelectric,[6, 7] piezoelectric,[8-10] and triboelectric[11-13] energy conversions have been among the most studied methods to achieve self-powered systems based on body temperature (static) and human movement (kinetic). Especially, thermoelectric and piezoelectric can be utilized reversely such as a cooler and an actuator, respectively. On account of their interesting properties, fundamental studies are being carried out.[7, 14] In addition, mechanical control of nanomaterials and systems has been studied to understand mechanical outputs in molecular level and utilize.[15-17] However, most wearable energy harvesting devices using these methods would likely be limited by the size of the displacement mass and the device position on the body for maximum displacement during human activity. Thus, human-based energy harvesting devices should be flexible, light, and stretchable because they have to be incorporated as wearable and wireless devices.

Recently, nanogenerators based on inorganic materials, such as lead zirconate titanate (PZT)[18-21] and ZnO,[22, 23] were reported to show high energy conversion efficiency and improved flexibility. However, the fabrication methods of these inorganic nanogenerators are too complex and require high temperature processes. The combination of organic electrodes and inorganic piezoelectric materials for flexible and stretchable devices is limited due to the high temperature calcination step. In addition, the inorganic materials are still fragile and restricted to be used under strain.[24, 25] Compared to inorganic piezoelectric materials, organic piezoelectric materials have the advantages of being flexible and light-weight.[9, 10, 26]

Among the organic materials, poly(vinylidene fluoride) (PVDF), $(–CH_2–CF_2–)_n$, and its derivatives are well known and widely applied to motion sensors, audio devices, actuators, and other technologies due to their high piezoelectric and pyroelectric properties.[27, 28] These energy-harvesting and sensor devices consist of a piezoelectric material layer and electrodes such as gold, aluminum, and indium tin oxide (ITO). Even though the organic piezoelectric material is flexible, the metal or oxide electrodes are not flexible enough to support the piezoelectric material.[29] Moreover, with the exception of the ITO,[30] such metal or oxide electrodes are generally not transparent. Recently, graphene was used as an electrode for piezoelectric device.[26] However, high temperature is required to synthesize the graphene and transferring the graphene electrodes is difficult to handle for large area. Only a small number of flexible and stretchable organic electrodes are known to support these organic piezoelectric materials, with the PEDOT:PSS and CNT composite electrode being one of the most successful examples. Nonetheless, their electrical conductivity is not high enough to harvest meaningful energy from human body movement, as a large loss in output power occurs due to the high resistance of the electrode.[31-33] Moreover, the large difference in surface energy between the hydrophilic PEDOT:PSS and hydrophobic piezoelectric layers may cause poor interfacial contact between the layers resulting in low fatigue properties over repeated human body movement. Thus, the electrical conductivity and surface energy of the electrode materials should be considered for highly efficient harvesting of dynamic energy from human movement through a piezoelectric conversion.

Herein, we present a simple and durable approach to fabricate highly conductive and flexible PEDOT electrode for piezoelectric

film devices consisting of PVDF. To match the surface energy of electrode materials with PVDF, we use PEDOTs doped with tosylate as an electrode material. Both the top and bottom electrodes of PEDOTs were directly coated by a solution casting polymerization (SCP) method using a solution of EDOT and oxidant (iron(III) tosylate) in the presence of a polymeric surfactant, which is compatible with conventional batch fabrication steps. All the processes including polymerization step were performed under T_g of the PVDF, even less than 70°C. Compared to the other inorganic piezoelectric process requiring high temperature, this all organic piezoelectric could be prepared at much lower temperature. Furthermore, we demonstrate that PVDF sandwiched with PEDOT electrodes can be applied to a highly efficient flexible energy harvester that converts human body movement into enough electricity to turn on an LED light. This mechanically durable and highly transparent thin-film generator, with its simple design, may be a critical step toward the realization of practical wearable devices, leading to new applications of highly conductive polymers as electrodes.

Experimental

Materials

A PVDF film and a PVDF film with PEDOT:PSS-CNT electrodes were purchased from the Fils Corporation. Here, CNTs were multiwall carbon nanotubes, and the film thickness of the PVDF was 85 μm. The piezoelectric coefficients were reported as 35 and 22 pC/N for d33 and d31, respectively. The PEDOT:PSS-CNT electrodes were removed by detaching each electrode from the three-layered PEDOT:PSS-CNT/PVDF/PEDOT:PSS-CNT film, and the central PVDF layer was used only as a piezoelectric film for the new PEDOT electrode in this study. The iron(III) chloride hexahydrate (purity 97%), *p*-toluenesulfonic acid monohydrate (purity > 98.5%), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEPG, weight-average molecular weight 2800), 3,4-ethylenedioxythiophene (EDOT) (purity 97%), pyridine (purity 99.8%), anhydrous methanol (purity 99.8%), and n-butanol (purity 99.8%) were purchased from Aldrich Chemicals. The anhydrous n-butanol was used after molecular sieve treatment to remove water. Other materials were used without any further purification. Iron(III) tosylate ($Fe(Tos)_3$) was prepared from $FeCl_3$ and *p*-toluenesulfonic acid monohydrate under the refluxing condition and purified as previously reported.[6, 34]

Preparation of the PP-PEDOT electrodes and energy generator device

Pyridine (13.54 mg) and PEPG triblock co-polymers (200 mg) were added into 1 g of oxidative solution containing 40 wt% of Fe-Tos in n-butanol. After stirring for 6 hours, the solution was sonicated for 10 min to make a homogeneous solution. The coating solution consisted of 52.8 wt% of the mixture solution of pyridine, PEPG, iron(III) tosylate, monomer, and 47.2 wt% of n-butanol. The molar ratio of pyridine: iron(III) tosylate: monomer was fixed at 0.55: 2.25: 1. Then, it was cooled before adding the EDOT monomers. A PVDF film with the dimensions 2.5×7.5 cm^2 was prepared by attaching it to a glass slide with tape. Because the PVDF film was itself flexible, we needed a rigid substrate on which to affix it for spin coating. The oxidative solution containing EDOT was spin coated onto the PVDF film, which was affixed onto glass flatly. Then, it was polymerized at 70°C with 35% humidity for 2 hours. The humidity was controlled by a closed chamber system containing a humidity-regulator and a hot plate. After cooling to room temperature, the samples were washed with ethanol to remove any residual oxidant, low molecular weight oligomers, and impurities. The sample was dried under N_2 flow and annealed on a hot plate at 70°C for 10 min. After detaching the PVDF film from a slide glass, the PP-PEDOT face was attached to a glass slide to fabricate another conducting polymer electrode on top of the PVDF layer with the SCP method. The same process was repeated to form the opposite-side PP-PEDOT electrode. The area of the final samples was 2×7 cm^2. A conducting metal wire was attached to all samples with silver paste.

Characterization

The thickness of the PVDF film was measured with a thickness profiler (Mitutoyo Corp. ID-C112). The electrical conductivity (σ) was measured with the standard four-probe method. The thickness of the electrodes was determined with an Alpha step profilometer (Tencor Instruments, Alpha-step IQ). For an application as an electrode, the electrode should attach to the substrate firmly. In particular, the electrode should maintain its original state and be attached to the substrate even when exposed to solvent or adhesive material. For this reason, the adhesion property of the electrodes to the PVDF surface was determined with a taping test (Fig. 1a). 3M tape was attached to the electrode, and pressure was applied to the entire area of the tape to ensure contact with the electrode. Then, the tape was detached from the electrode by pulling from one edge of the tape. This process was repeated 3 times. The surface wettability was determined with distilled water, measuring the ethylene glycol drop contact angle using the contact angle meter-CAM 101 model (KSV Instruments Ltd., Finland). UV-vis-NIR absorption spectroscopy was performed with a PerkinElmer Lambda 750. Field-emission scanning electron microscopy (FE-SEM) was performed using JEOL-JSM-6700F with a thin platinum coating to image the interface of the electrode and the PVDF film. A Keithley 6485 picoammeter, a Keithley 2842A nanovoltmeter, and a Tektronix DPO2024 oscilloscope were used for low-noise and precise current/voltage measurements to detect currents and voltages generated by the all-organic-film-type generators. Uniform mechanical pressing and stretching were performed by a UTM (YEONJIN TopTac 2000). Fourier Transform Infrared (FT-IR) spectra were obtained with a TENSOR 37 (Bruker). A sponge-type double-sided tape was attached to the sample to prevent leakage through the metal holder or loss of the sample from the holder.

Results and Discussion

A thin film energy harvester consists of three-layered films in which the piezoelectric film (PVDF) is sandwiched between two electrodes. To reduce interfacial resistance between the electrode and the PVDF, PEDOT was directly coated on top of the piezoelectric film (area = 2×7 cm^2) via a SCP method at 70°C under 35% humidity. The solution for this process consisted of the monomer (EDOT), pyridine, PEPG triblock co-polymer, and

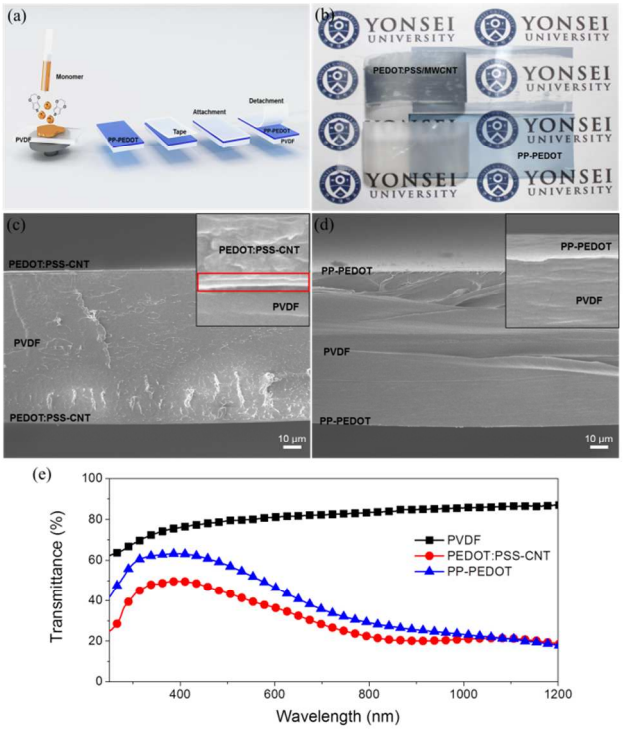

Fig. 1 (a) A schematic image of the taping test to verify the adhesion property and stability of electrodes. (b) A photograph of the adhesion test between the PEDOT:PSS-CNT and PP-PEDOT electrodes and PVDF. Cross-sectional FE-SEM images of the interface between the PEDOT:PSS-CNT and PP-PEDOT electrodes and PVDF. Cross-sectional FE-SEM images of the interface between the PVDF film and (c) PEDOT:PSS-CNT and (d) PP-PEDOT, respectively (Inset: 1×1 μm^2 enlarged images). (e) UV−vis−NIR spectra of the pristine PVDF, double-sided electrodes of the PEDOT:PSS-CNT piezoelectric film, and those of the PP-PEDOT-substituted piezoelectric film.

iron(III) tosylate in n-butanol. The resultant PEDOT, reported as PP-PEDOT previously,[6] is doped with tosylate and thus water insoluble. The thickness and the electrical conductivity of the PP-PEDOT film coated on top of the PVDF layer were 120 nm and 1340 S/cm, respectively. The conductivity of the fabricated PP-PEDOT was among the highest and thus could be useful as an electrode for piezoelectric devices. On the other hand, the PEDOT:PSS-CNT electrodes on the PVDF film showed an electrical conductivity (σ) of 1.9−8.3 S/cm, which was much lower than that of PP-PEDOT determined by the four-probe method.

The stability of the β-phase crystalline form of PVDF during the polymerization of the EDOT monomers was confirmed by FT-IR (Fig. S1). The spectra of the original PVDF and sample film, after removal of the PP-PEDOT electrode, were obtained. The bands assigned as β-phase crystalline appear distinctly at 846, 1285, and 1431 cm^{-1} in the PVDF film.[9] These bands were well maintained, and no significant difference was observed for the sample that had the PP-PEDOT electrode removed.

Interestingly, the PP-PEDOT layer was grown on PVDF layer with high adhesion without detachment under repeated film test, as illustrated in Fig. 1a. While most of the PEDOT:PSS-CNT film detached from the PVDF surface (Fig. 1b), the PP-PEDOT

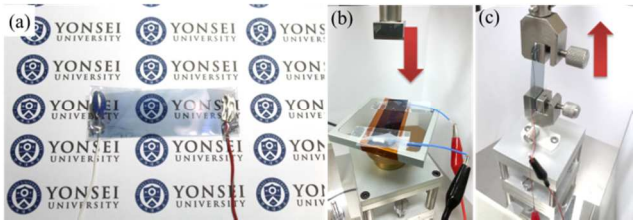

Fig. 2 Photographic images of (a) a piezoelectric film device sample with PP-PEDOT electrodes, (b) mechanical press measurement system for applying a precise and uniform force of 1 N, and (c) output power measurement system for applying mechanical stretching force of 380 to 800 mN and displacement of 0.125 to 0.372 mm.

film was well adhered onto the PVDF surface after repeating the tape detachment test three times. This strong adhesion characteristic of the PP-PEDOT electrode was also confirmed from the cross-cut image of the three-layered film by FE-SEM, shown in Fig. 1c, d. The interface between the PVDF and electrode had a tight interface without any noticeable interfacial gap. On the other hand, the interfacial gap between the PEDOT:PSS-CNT film and PVDF was much more distinct, with a large gap (~40 nm), making tape detachment easy (Fig. 1c).

The strong adhesion characteristic of the PP-PEDOT electrode may arise from the surface energy matching with the PVDF surface. The surface energy of PVDF was determined to be 36.6 mJ/m^2, which is more matched to that of PP-PEDOT (41.1 mJ/m^2) than that of PEDOT:PSS-CNT film (21.9 mJ/m^2).[35] Thus, the smaller difference in surface energy ($\Delta\gamma$ = 6.5 mJ/m^2) for the PP-PEDOT electrode with PVDF relative to the PEDOT:PSS-CNT ($\Delta\gamma$ = 14.7 mJ/m^2) films could lead to better adhesion to the PVDF surface. Moreover, direct SCP of the monomeric EDOT on PVDF could enhance the adhesion of PEDOT because of the bonded interface from the polymerization of the wetted monomers on the surface of the PVDF. This high adhesion of the PP-PEDOT electrodes to the PVDF film was strong enough to produce a durable piezoelectric film device of PP-PEDOT/PVDF/PP-PEDOT under repeated bending and twisting condition.

The transmittance of a bare PVDF film with a thickness of 85 μm, without any electrodes, was 80% at 550 nm. The bare PEDOT:PSS-CNT and PP-PEDOT electrode had similar transmittances in the near IR region beyond 1100 nm, as shown in Fig. 1e. Interestingly, in the visible and NIR range below 1100 nm, the PP-PEDOT electrode showed higher transparency. The transmittance of the PEDOT:PSS-CNT electrodes was very low, showing an average transmittance of 39.8% for the entire visible light region (400 nm to 700 nm). On the other hand, with the PP-PEDOT electrodes, the transmittance was much higher, showing an average transmittance greater than 51.5% transmittance for the visible light region. The as-prepared PEDOT film (PP-PEDOT) was partially doped, with the degree of doping as 24.1 ± 0.4%.[5] Thus, the energy harvester (PP-PEDOT/PVDF/PP-PEDOT) showed a relatively higher transparency (51.5%) than the PEDOT:PSS-CNT system (39.8%). Considering that the average visible light transparency of the PVDF was 79.8%, the average decrease in transparency from the two PP-PEDOT electrodes was 35.5%, which was smaller than the PEDOT:PSS-CNT system (50%).

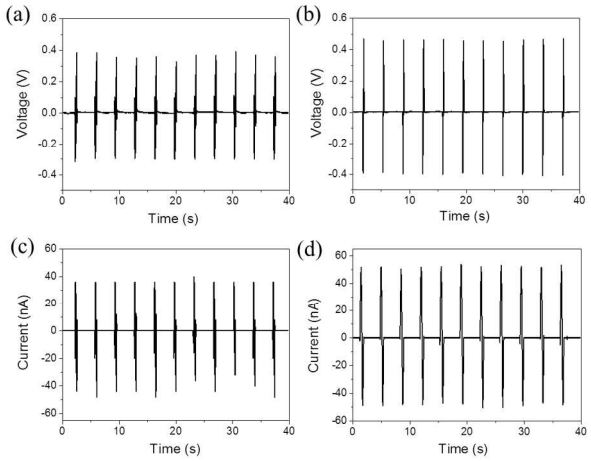

Fig. 3 (a) Measured output voltage and (c) measured output current of PEDOT:PSS-CNT. (b) Measured output voltage and (d) measured output current of the PP-PEDOT electrode-substituted PVDF film with an applied force of 1 N from the mechanical press.

To measure the piezoelectric property of the PP-PEDOT-substituted PVDF film, the measurement system was set up as shown in Fig. S2. The output voltage was obtained by a nanovoltmeter and oscilloscope. The picoammeter signal was directly obtained using the connected oscilloscope to detect the piezoelectricity accurately. Fig. 2a shows the prepared piezoelectric sample for measurement. Various controlled forces were applied to the sample using the UTM force generator, to press (Fig. 2b) and stretch out (Fig. 2c) the piezoelectric films. As shown in Fig. 2b, the bottom area of the pressing tool is 4 cm^2, which corresponds to the active area of the piezoelectric device for press experiments.

The measured output voltage of the PP-PEDOT film device from uniform mechanical stress was higher than that of the PEDOT:PSS-CNT devices. When the mechanical press was applied to the piezoelectric samples, the remnant polarization of the PVDF increased; the increased electrostatic states, in turn, drive the electrical flow of the electrodes. The recorded peak to peak output voltage was 0.86 V when the applied force was 1 N. The output voltages with PP-PEDOT were increased about 27% compared to that with PEDOT:PSS-CNT (0.68 V) in the same condition and using same-sized samples (Fig. 3a, b). The UV-vis-NIR spectra of PP-PEDOT and PEDOT:PSS-CNT showed that the doping level and charge carrier concentration had similar states. Even though the PP-PEDOT electrode has a similar doped state to the PEDOT:PSS-CNT system, it has low electrical resistance. The measured peak to peak current was also about 20% larger for the PP-PEDOT system (101.4 nA), as shown in Fig. 3c, d. Because the mechanical press was applied to the center of the sample, there should be a loss of output signal when the output generation is propagated over the entire area of the electrode. In the case of the PP-PEDOT system, the smaller loss of output voltage may be attributed to the high electrical conductivity of the piezoelectric device electrodes relative to that of the PEDOT-PSS-CNT system. Moreover, the tight adhesion of the PP-PEDOT film to PVDF may result in a higher output voltage and current than that of the PEDOT:PSS-CNT system.

The electricity was more harvested from the piezoelectric film

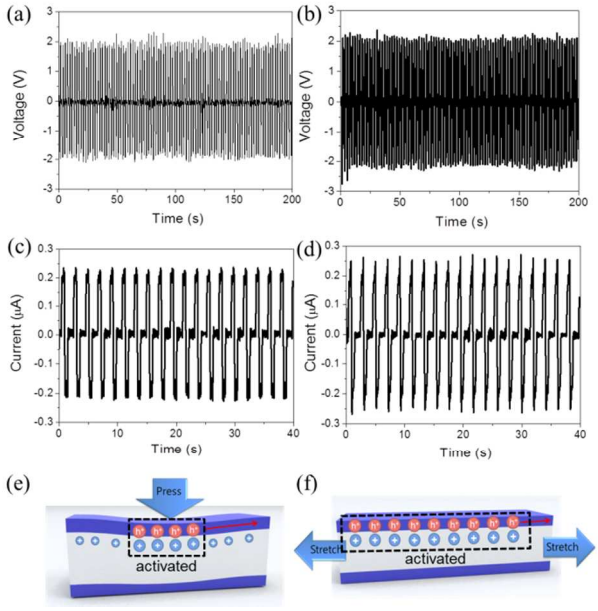

Fig. 4 (a) Measured output voltage and (c) measured output current of PEDOT:PSS-CNT. (b) Measured output voltage and (d) measured output current of the PP-PEDOT electrode-substituted PVDF film from the mechanical stretch (450 mN). Schematic images of drift hole movement and output power generation from (e) mechanical press and (f) mechanical stretching

device with the PP-PEDOT electrodes upon stretching of the film. A piezoelectric sample was held at both ends (top and bottom) as shown in Fig. 2c. From the mechanical stretching, the output voltage was much more enhanced compared to the above mechanical press (Fig. 4a, b). The PEDOT:PSS-CNT sample had an output voltage of 3.93 V, with a peak-to-peak intensity for the applied strain of 0.24%. The PP-PEDOT-substituted piezoelectric film had a higher output voltage of 4.28 V (peak to peak) for the same strain. The output voltage obtained by a nanovoltmeter, without any break time during the repeatable stretching, increased about 9% by changing the electrodes from PEDOT:PSS-CNT to PP-PEDOT. The output voltage of this piezoelectric device with reversed connection was also obtained to show that the observed results are truly from the piezoelectric part (Fig. S3). In the case of the output current, these values were measured by an oscilloscope through a picoammeter to obtain more accurate values. We can obtain values for more than 5,000 points for 40 s of recording time. The PP-PEDOT sample exhibited 0.50 μA (peak to peak) and PEDOT:PSS-CNT 0.45 μA (peak to peak) for a stimuli of 450 mN, respectively (Fig. 4c, d). The value for the PP-PEDOT device was 12% higher than that of the PEDOT:PSS-CNT device. Compared to the enhancement of the output energy from the mechanical press in the PP-PEDOT device as referenced to the PEDOT:PSS-CNT device, that from the mechanical stretching was smaller. In the case of energy generation from the mechanical press, the output voltage increased by more than 28%, and the current increased by as much as 20% in the PP-PEDOT device as compared to the PEDOT:PSS-CNT device. When a piezoelectric film device was placed on a plate under pressure by a mechanical press tool, only the center of the sample was

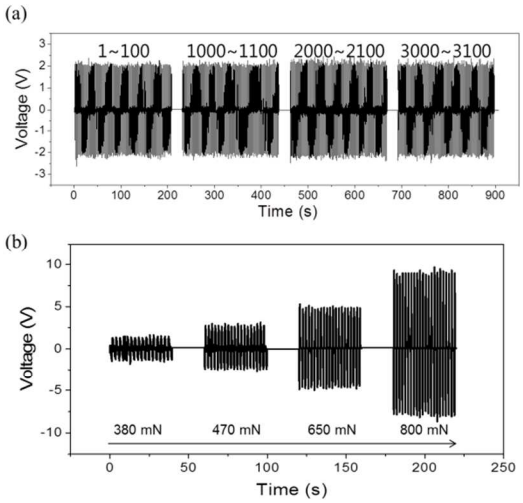

Fig. 5 (a) Measured output voltage of the PP-PEDOT electrode-substituted PVDF film from more than 3,000 mechanical stretching motions (450 mN) for a durability test. (b) Measured output voltage of the PP-PEDOT electrode-substituted PVDF film with different amounts of mechanical stretching.

pressurized (Fig. 4e). Then, the remnant polarization of PVDF was changed, forcing the charge carriers such as holes of the PP-PEDOT electrodes to drift from the center where the press was applied to the edge of the sample[26]. The drift holes should pass through the electrodes. Because the mechanical press was applied to the center of the sample, there should be a loss of output generation when the output signal is propagated over the entire area of the electrode. In the case of the PP-PEDOT device, the smaller loss in the output voltage may be attributed to the high electrical conductivity and high adhesion of the PEDOT in piezoelectric device electrodes compared to the PEDOT:PSS-CNT device. The loss of output energy increases if the electrode has a high electrical resistance. On the other hand, in the case of energy harvesting by the stretching process (Fig. 4f), the whole sample from the top to bottom was stretched, and the number of drift holes also increased. The loss through the electrode, especially in the area of the activated region, was much smaller compared to energy harvesting using pressure. In other words, the output voltage and current generated from the stretching process were not affected as much as the output values from the mechanical press. Therefore, the enhancement of generated output energy by mechanical press in the PP-PEDOT device, compare to the PEDOT-PSS-CNT device, is much higher than that generated by the mechanical stretching (Table 1).

Strain was applied to the PP-PEDOT piezoelectric film device during the mechanical stimuli. The deformation of the samples generated the same output energy reproducibly over repeated cycles. To supply a uniform signal to electronic devices as an energy harvester, the samples should be sustainable to the external stimuli. For this reason, the PVDF should itself be durable, and the electrode of a piezoelectric film device should be stable for repeated deformation and dynamic human motion. The top and bottom of the PP-PEDOT sample were fixed in holders, as shown in Fig. 3d. The top holder moved up and down repeatedly at a rate of 0.5 mm/s, and the maximum force applied at the highest position was 450 mN. The stretching processes

Table 1 The transmittance, electrical conductivity, thickness, measured output values, and output efficiencies of the PEDOT:PSS-CNT and PP-PEDOT films at room temperature.

Sample	PEDOT:PSS-CNT	PP-PEDOT **(Enhanced:%)
*Decrease transmittance (%) (double-sided electrodes at 400 and 550 nm)	26.5 / 40.2	12.9 / 27.7
Electrical conductivity (S/cm)	1.9-8.3	1250-1340
Thickness (μm)	0.8-0.95	0.11-0.13
-Transmittance of 85 μm thick PVDF were 76.1 and 80.0 % at 400 and 550 nm, respectively.		
Mechanical press applied (peak to peak value)		
Output Voltage (mV)	674	864 **(28)
Output Current (nA)	84	101 **(20)
***Output efficiency (mV/N)	67	86 **(28)
Mechanical strain applied (380 mN) (peak to peak value)		
Output Voltage (V)	2.40	2.72 **(13.1)
Output Current (nA)	96	112 **(16.2)
***Output efficiency (V/N)	6.23	7.06 **(13.3)

*Decrease transmittance: decrease of transmittance compared to the transmittance of the original PVDF film by applying double-sided electrodes
** Enhanced (%): relative increase of output voltage and current of PP-PEDOT compared to PEDOT:PSS-CNT system
***Output efficiency was calculated from output voltage (V) and maximum applied force (N).

were repeated more than 3000 times to confirm the durability of the sample. Fig. 5a shows the output voltage obtained for 100 cycles for every 1000 stretching motions. The measured output voltage was well maintained after 3000 repeated stretching motions. The measured output current was also obtained (Fig. S4). The calculated strain value for the stretching test was 0.24%. Because the conducting polymer electrodes can endure more strain with a nanometer thickness range, they can maintain the piezoelectric output without a decrease even after 3000 repeated stretching motions. To support the durability of the PP-PEDOT electrode, electrical conductivities were obtained under different applied stretching strain (Fig. S5). Electrical conductivities were well maintained even at the applied stretching strain higher than 1%.

By increasing the stretching force, a higher output voltage was obtained (Fig. 5b). The output current is shown in Fig. S6. As the strain increased under a force of between 380 and 800 mN, so did energy harvesting from the piezoelectric film device with the PP-PEDOT electrodes. With 800 mN, each stretching and releasing generated more than 16 V. The output current also increased up to 1.6 μA. The output voltage and current of the piezoelectric film device with the PEDOT:PSS-CNT electrodes are compared in Fig. 6, which shows that the PP-PEDOT electrode system generates more energy than does the former. The improvement in electricity harvesting could be estimated from the linear fit in Fig. 6, where the slope indicates the output efficiency of energy harvesting. In the plot of the output voltage against strain (%), the slopes were 32.3 and 30.8 V/N for PP-PEDOT and PEDOT:PSS-CNT, respectively. Likewise, the slopes for output current were 3.53 and 3.20 μA/N, respectively. With a maximum force of 380 mN, the output voltage and current for the PP-PEDOT electrode were 13% and 16%, respectively, higher than the PEDOT:PSS-CNT electrodes. The average output voltage and current enhancements for the PP-PEDOT electrode against four different strain regions were 7.6% and 11%, respectively. The results of the energy

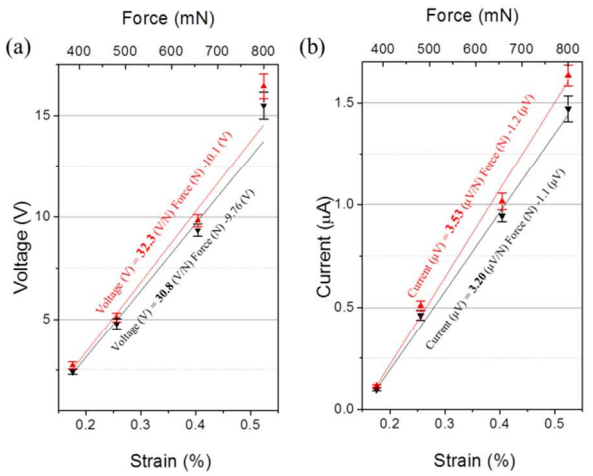

Fig. 6 (a) Measured output voltage of PEDOT:PSS-CNT and PP−PEDOT, (b) measured output current of PEDOT:PSS-CNT and PP−PEDOT electrodes substituted PVDF film from the mechanical stretching. The slopes (V/N, μA/N) were obtained from linear fits to the experimental results. (PEDOT:PSS-CNT: black, PP−PEDOT: red)

generation from the mechanical press and strain are summarized in Table 1. With the same applied forces, more outputs were generated from the PP-PEDOT electrode. The improvement in electricity harvesting in the PP-PEDOT electrode could be clearly confirmed by comparing the output efficiency (V/N) against the PEDOT:PSS-CNT electrodes. In addition, a resistor decade box was used to investigate the dependence of effective output power on the external load. As shown in Fig. S7, the maximum current was decreased with increasing resistance. On the other hand, the voltage across the load was increased. Consequently, the power density on the load reached a maximum value of 8.34 mW/m^2 at a resistance of ~ 9 MΩ. To obtain the power output efficiency from the entire device, the maximum electrical energy was calculated and divided by the input mechanical energy[36]. The practical energy harvesting efficiency (See also a description in Supplementary Information) determined as 0.47% of the PP-PEDOT device with PVDF is well matched to the reference value of the PVDF film devices[37].

Taking advantage of the very high energy harvesting from stretching, we applied the PP-PEDOT electrode with the PVDF film to a lighting system connected through homemade circuitry that included an LED lamp, capacitor, switch module, and rectifying bridge. The AC outputs were converted to DC power through the rectifier and stored in the capacitor. The measured output voltages, before and after rectification, are shown in Fig. S8. The 2×7 cm^2 PP-PEDOT electrode sample was placed in the mechanical stretching tool for generating output power. Each side of the sample was fixed in a holder; thus, the active area was 2×4 cm^2. The fixed sample was stretched out 100, 1000, 3000, and 5000 times to operate under a uniform stretching force (800 mN) and to charge the capacitor. Then, the switch connecting the charged capacitor and the LED lamp was pressed by hand to capture photographic images. From the photographic images shown in Fig. 7, one can clearly see that the LED light was lit brilliantly by the electricity generated from the stretching. By

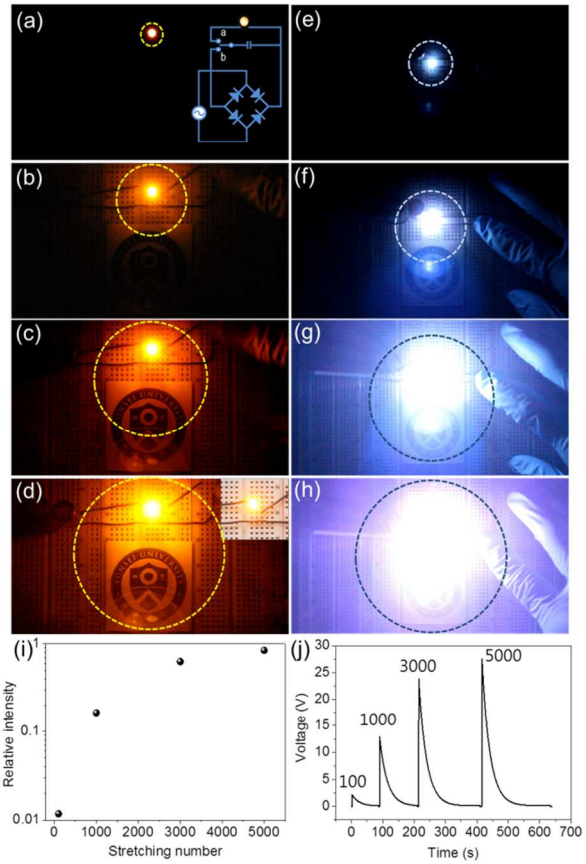

Fig. 7 Photographic images of the light incorporated into the circuit. As the number of stretching motions increased, the light powered by energy generated from the PP-PEDOT-substituted piezoelectric film grew brighter. (a) 100, Inset: the circuit for a piezoelectric generator connected to charge a capacitor that powers the LED lamp. (b) 1000, (c) 3000, and (d) 5000 stretching motions. Inset: photographic image of the LED in a bright background at the moment of being lit. Photographic images for the white LED lamp with the same stretching process applied (e) 100, (f) 1000, (g) 3000, and (h) 5000 times. (i) Relative intensities of the LED light for different stretching times. (j) The output voltage and discharge data of the capacitor for different repeated stretching processes.

increasing the number of stretching motions, the brightness increased, and the "Yonsei Univ." marker positioned under the LED lamp in the circuit was illuminated more brightly and could be read more easily.

In addition, the flexible and durable PP-PEDOT electrodes were directly applied to energy harvesting from the activity of human elbow. The piezoelectric device with PP-PEDOT electrodes was attached to an elbow. When we folded the elbow, the piezoelectric device was stretched and generated an output voltage of 650 mV (peak-to-peak). The PP-PEDOT electrodes with the PVDF film were fitted onto the elbow and remained stable despite humidity and sweat from the human body. In this way, we demonstrated the performance of the piezoelectric film with the PP-PEDOT electrodes (a video clip Supplementary Information).

Since the surface energy matching PP-PEDOT electrodes is transparent and highly conductive, it could be applied into wide

range of energy harvesting including triboelectric generators or hybrid type of energy generators that combine, for example, piezoelectric with triboelectric layers. Further studies on these application potential are in progress and hopefully will be published soon.

Conclusions

In summary, a more transparent and efficient piezoelectric film device could be obtained using a highly conductive polymer, PP-PEDOT, as electrodes without a high temperature process and a complex transferring of electrode. The surface energy of the PP-PEDOT electrode was matched well to that of the PVDF, allowing highly adherent and mechanically stable interface between them. The piezoelectric PVDF film with PP-PEDOT electrodes was 28% more transparent and generated 27% more output voltage under mechanical pressure compared to that with PEDOT:PSS-CNT electrodes. When mechanical stretching was applied, the output voltage and current values were about 7.6% and 11.1% higher, respectively, with the PP-PEDOT electrodes than those with PEDOT:PSS-CNT electrodes. This all-organic PP-PEDOT piezoelectric device was flexible, stretchable, and mechanically durable, with cyclability more than 3000 stretching motions. This allowed a mechanical-lighting system and a human body energy harvester. LED lamps were lit brilliantly by the energy generated from the PP-PEDOT piezoelectric device, with high performance and durability. The piezoelectric device with PP-PEDOT electrodes was attached to an elbow generated an output voltage of 650 mV (peak-to-peak) when the elbow was folded. We believe that the all-organic piezoelectric device with the highly conductive and surface energy matching PP-PEDOT electrodes is very promising for harvesting energy from natural resources and human body movements.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, characterization, FT-IR and output values. See DOI: 10.1039/C3TA00000x

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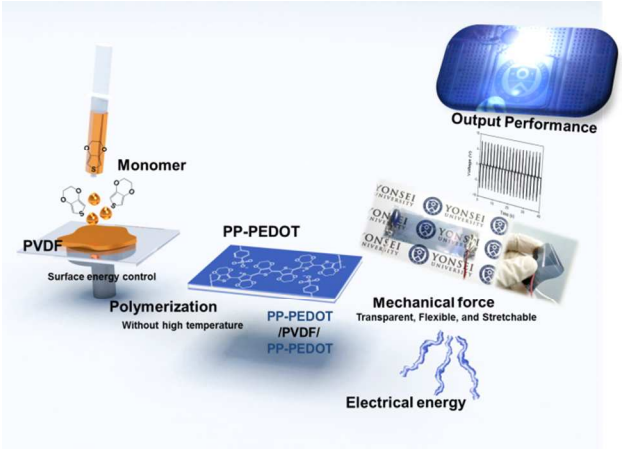
TOC



Highly conductive, transparent, surface energy matched, and flexible PEDOT electrodes for all organic piezoelectric device show an enhanced piezoelectric conversion efficiency.