

Highly Conductive, Stretchable, and Transparent PEDOT:PSS Electrodes Fabricated with Triblock Copolymer Additives and Acid Treatment

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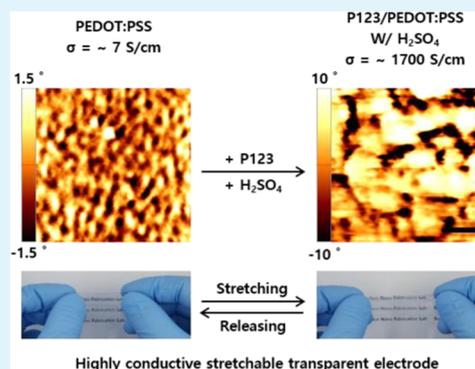
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Supporting Information

ABSTRACT: Here, we report on a highly conductive, stretchable, and transparent electrode of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) fabricated via modification with triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEO₂₀-PPO₇₀-PEO₂₀, Pluronic P123), and post-treatment with sulfuric acid. The fabricated electrode exhibits high transparency (89%), high electrical conductivity (~ 1700 S/cm), and minimal change in resistance ($\sim 4\%$) under repetitive stretch–release cycles at 40% tensile strain after stabilization. P123 acts as a secondary dopant and plasticizer, resulting in enhanced electrical conductivity and stretchability of PEDOT:PSS. Furthermore, after sulfuric acid post-treatment, P123 helps the electrode to maintain its stretchability. A successful demonstration of the stretchable interconnection was shown by stretching the P123-modified PEDOT:PSS electrodes, which were connected with light-emitting diodes (LEDs) in series.

Finally, a stretchable and transparent touch sensor consisting of our fabricated electrodes and an LED array and stretchable semitransparent supercapacitor were presented, suggesting a great potential of our electrodes in the application to various deformable devices.

KEYWORDS: stretchable transparent electrode, PEDOT:PSS, triblock copolymer, sulfuric acid treatment, stretchable electronics



1. INTRODUCTION

With the increasing demand for wearable healthcare monitoring systems and the development of related industries, research on electronic systems that can interact with the human body has gained attraction. Considerable efforts have been made to develop materials that are mechanically and electrically stable under various deformations in accordance with body movements.¹ Stretchable transparent electrodes are one of the fundamental elements of deformable electrical devices, since they themselves are useful and are essential in various optical displays^{2,3} and photovoltaic devices.^{4–6}

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is the most widely used conductive polymer owing to its thermoelectric properties,^{7,8} electrical conductivity, transparency, and solution processability. PEDOT is a hydrophobic conjugated polymer, and its hydrophilic PSS segment counterpart disperses PEDOT into aqueous solutions. However, the pristine PEDOT:PSS thin film is sensitive to humidity,⁹ and critically, it has limited electrical conductivity (<10 S/cm) and low yield strain ($<6\%$).¹⁰ By introducing additives or post-processing with various solutions, the electrical conductivity and stretchability of PEDOT:PSS films can be enhanced. Additives

can weaken ionic interactions between PEDOT and PSS chains, thereby increasing conductivity, and they sometimes have a plasticizing effect that increases the stretchability of the PEDOT:PSS film. Typical examples of additives include polymers and polar solvents, such as poly(ethylene glycol),⁴ polyethylenimine,¹¹ dimethyl sulfoxide,^{12,13} ionic liquids,^{14–16} and surfactants, such as Zonyl,^{13,17–19} Triton X-100,²⁰ and sodium dodecyl sulfate.²¹ Post-treatment methods can also dramatically improve the conductivities of PEDOT:PSS films by inducing composition and structural changes, using solvents such as alcohol,^{6,22} surfactant solutions,²¹ bases,^{23,24} and acids.^{24–29} For instance, the conductivity of the PEDOT:PSS film was increased to ~ 4000 S/cm by soaking the film in concentrated sulfuric acid.²⁵

Current research on stretchable PEDOT:PSS electrodes focuses on simultaneously improving conductivity and stretchability, since these two properties are usually complementary. Conductivity enhancement is often achieved by increasing the

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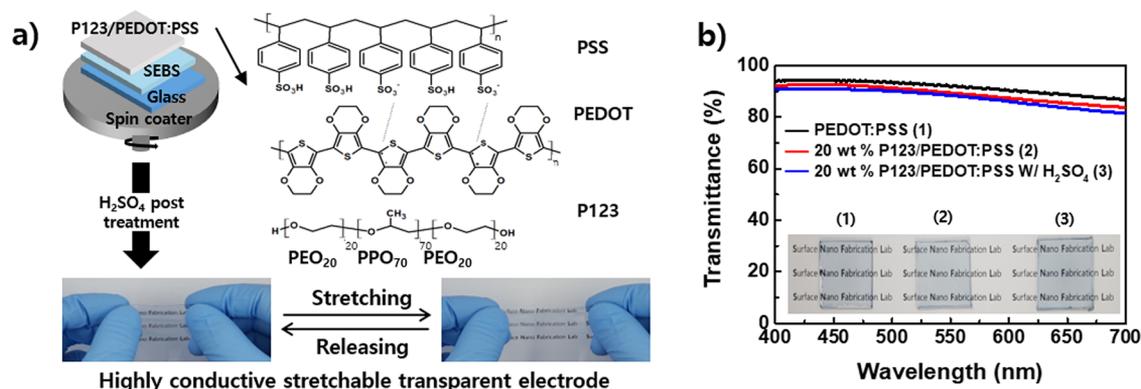


Figure 1. (a) Schematic showing fabrication of stretchable transparent electrode. (b) Transmittance spectra of PEDOT:PSS films fabricated with various modifications: (1) pristine PEDOT:PSS; (2) 20 wt % P123/PEDOT:PSS; and (3) 20 wt % P123/PEDOT:PSS post-treated with sulfuric acid. The inset shows photographs of highly transparent $2.5 \times 2.5 \text{ cm}^2$ PEDOT:PSS films.

crystallinity of PEDOT, making the film susceptible to deformation. Moreover, for stretchable electrodes, it is important to maintain their high conductivity even under external tensile strain. Post-treatment using methanesulfonic acid was reported to increase the conductivity of stretchable PEDOT:PSS film to 2890 S/cm, whereas the resistance of the film increased to 30 times under 30% tensile strain.²⁶

Herein, we demonstrate a highly conductive, stretchable, and transparent electrode fabricated based on PEDOT:PSS and an amphiphilic triblock copolymer called a “poloxamer”, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEO₂₀-PPO₇₀-PEO₂₀, Pluronic P123). The fabricated electrode showed high transmittance (89%), high durability, and minimal change in resistance when stretched over 1000 stretch–release cycles at 40% tensile strain. The electrode post-treated with sulfuric acid exhibited a high conductivity of $\sim 1700 \text{ S/cm}$ and 4% resistance increment during stretching up to 40% after irreversible increase of resistance ($\sim 26\%$). The enhanced performance of our PEDOT:PSS film is superior to the existing PEDOT:PSS electrodes using polymers, surfactants, and various solvents and comparable to the ones of the currently reported ionic liquid modification, which also showed high conductivity and stretchability.

2. EXPERIMENTAL SECTION

2.1. Materials. PEDOT:PSS (Clevios PH1000, PEDOT:PSS = 1:2.5) was purchased from Heraeus. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) ($M_n \sim 5800$, PEO₂₀-PPO₇₀-PEO₂₀, Pluronic P123, P123), (3-aminopropyl)-triethoxysilane (APTES, 99%), poly(vinyl alcohol) (PVA, $M_n = 89000$ – 98000), and phosphoric acid ($\geq 85 \text{ wt \%}$ in H₂O, $\geq 99.999\%$ trace) were purchased from Sigma-Aldrich. Styrene–ethylene–butylene–styrene (SEBS, Tuftec H1052) was supplied by Asahi Kasei elastomer. Sulfuric acid (ACS, 95.0–98.0%) was purchased from Alfa Aesar.

2.2. Fabrication of P123-Modified PEDOT:PSS Stretchable Transparent Film. A 200 mg/mL solution of SEBS dissolved in toluene was spin-coated at 300 rpm for 3 min onto $2.5 \times 2.5 \text{ cm}^2$ glass slides, which had previously been rinsed with acetone, deionized (DI) water, ethanol, and isopropanol. The spin-coated slides were then annealed at 80 °C for 30 min on a hot plate. The PEDOT:PSS solution was mixed with various concentrations of P123 and stirred at 800 rpm overnight. The mixed solution of PEDOT:PSS and P123 (P123/PEDOT:PSS) was cooled to 5 °C and spin-coated at 2000 rpm for 1 min onto ultraviolet (UV)–ozone-treated SEBS substrates, followed by annealing at 120 °C for 15 min. Pristine PEDOT:PSS could not be

coated onto an SEBS substrate since the pristine PEDOT:PSS cracked during annealing.

2.3. Post-Treatment of PEDOT:PSS Film with Sulfuric Acid.

The prepared P123/PEDOT:PSS film was soaked in concentrated sulfuric acid for 1 min and subsequently washed with DI water. The post-treated film was annealed for 10 min at 90 °C on a hot plate. Hereinafter, the nontreated film and the post-treated film with sulfuric acid are denoted as W/O H₂SO₄ and W/H₂SO₄, respectively.

2.4. Fabrication of a Stretchable Touch Sensor. To fabricate the bottom and top electrodes for the stretchable touch sensor, a 20 wt % P123/PEDOT:PSS film post-treated with sulfuric acid was prepared on a $5 \times 5 \text{ cm}^2$ SEBS-coated glass substrate. The bottom electrode was patterned using oxygen reactive ion etching, and nine light-emitting diodes (LEDs) were positioned on the bottom electrode connected by silver paste. The top electrode was used as is to show its high transparency. For electrical separation between the top and bottom electrodes, a half-cured, 2 mm thick poly(dimethylsiloxane) (PDMS) film was prepared with a base-to-curing agent ratio of 10:1. After perforating the PDMS, aligned with the LED array and touch areas, it was attached to the bottom and top electrodes. Then, the edges of the sensor were covered with PDMS and were cured for 20 min. Finally, the sensor was detached from the glass substrate.

2.5. Fabrication of a Stretchable Semitransparent Supercapacitor. Sulfuric acid-post-treated 20 wt % P123/PEDOT:PSS films were used as current collectors, and for the electrode, carbon nanotubes (CNTs) were spray-coated on the PEDOT:PSS film. A gel electrolyte was prepared by mixing 15 mL of H₃PO₄ and 15 g of PVA with 150 mL of DI water. The mixture was stirred at 150 °C in a hot plate. When PVA/H₃PO₄ gel became transparent, the gel was drop-casted on the bottom electrode and another electrode was stacked on top after it was dried enough.

2.6. Characterization. To examine the electrical conductivities, P123-modified PEDOT:PSS films were prepared on silica substrates, which had been functionalized with a self-assembled monolayer of APTES for 4 h to prevent the P123/PEDOT:PSS layer from being separated from the substrate during the post-treatment process. Sheet resistance was measured using the four-probe method (MStech, M4P205), and the film thickness was measured using a DektakXT stylus profiler (Bruker). The electrical conductivities were calculated by the following equation

$$\text{electrical conductivity (S/cm)} = \frac{1}{\text{sheet resistance } (\Omega/\text{sq}) \times \text{thickness (cm)}} \quad (1)$$

and the standard deviations were obtained using three different samples for each P123 concentration.

Atomic force microscopy (AFM) images were acquired in noncontact mode using a Park XE-100 atomic force microscope (Park Systems).

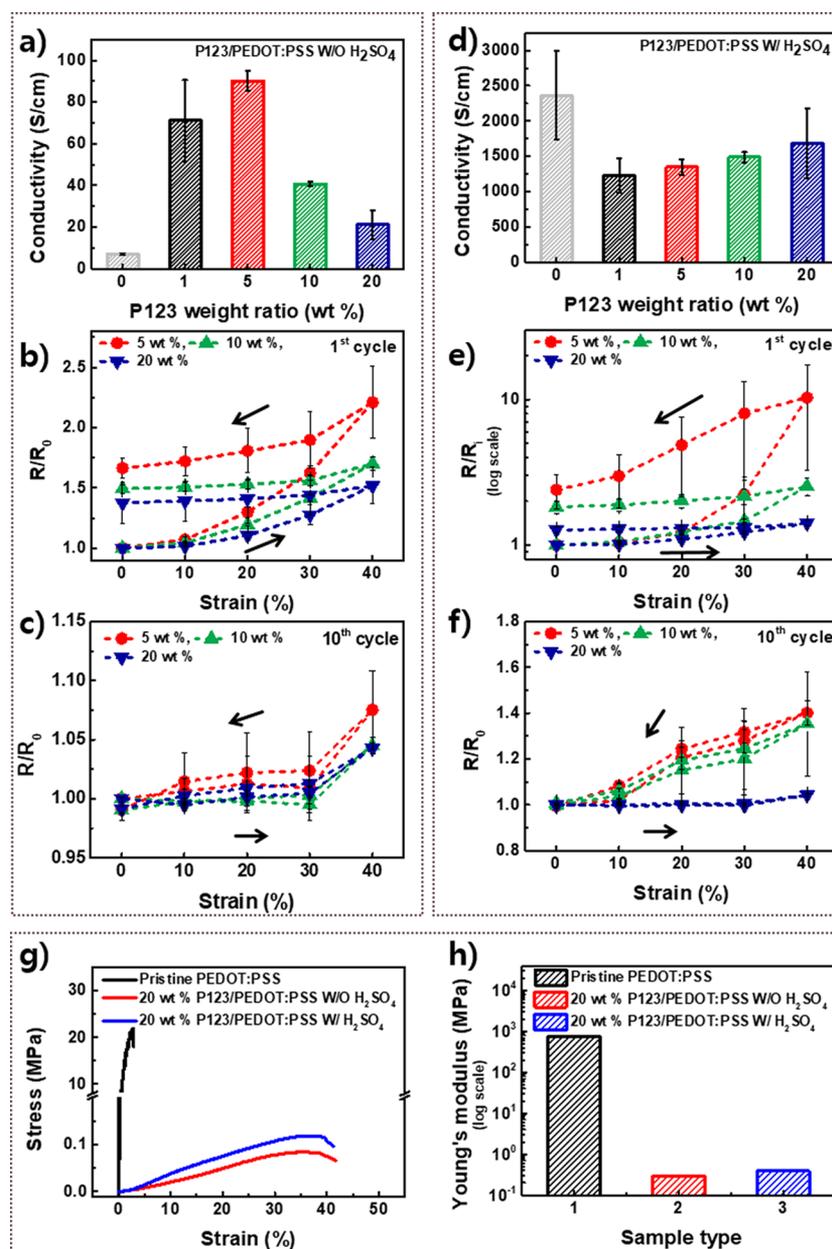


Figure 2. (a) Electrical conductivities of PEDOT:PSS films prepared with various concentrations of P123. Normalized resistance (R/R_0) versus strain curves of PEDOT:PSS electrodes prepared with various concentrations of P123 at the (b) 1st cycle and (c) 10th cycle after stabilization. (d) Electrical conductivities of sulfuric acid-post-treated PEDOT:PSS films prepared with various concentrations of P123. (e) R/R_0 versus strain curves of PEDOT:PSS electrodes after sulfuric acid post-treatment prepared with various concentrations of P123 at the (d) 1st cycle and (f) 10th cycle after stabilization. (g) Stress–strain curves and (h) Young's modulus of free-standing pristine PEDOT:PSS, 20 wt % P123/PEDOT:PSS films with and without sulfuric acid post-treatment. Here, R_0 , R , and R are the resistances measured before initial stretching, resistance at 0% strain after each cycle, and resistance with applied strain, respectively.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy data were obtained using a Nicolet iS 10 (Thermo Fisher Scientific). X-ray photoelectron spectroscopy (XPS) data were taken using X-TOOL (ULVAC-PHI), where the background was subtracted using the Shirley model, and the obtained binding energy was calibrated with the C 1s peak at 284.8 eV. The PEDOT:PSS film was electromechanically characterized using a custom-built stretching machine and a probe station (B1500A, Agilent Technologies).

The luminance of the LED was measured with a TES 1330A lux meter under 3 V at 10 cm. The stretchable transparent touch sensor was operated under 5 V.

The electrochemical properties of stretchable semitransparent supercapacitor were measured by means of cyclic voltammetry (CV) using an electrochemical analyzer (Ivium Technologies, CompactStat).

3. RESULTS AND DISCUSSION

The fabrication scheme of the stretchable and transparent PEDOT:PSS film is given in Figure 1a. The P123/PEDOT:PSS solution was spin-coated onto the SEBS elastomer substrate. The spin-coated films were soaked in concentrated sulfuric acid for 1 min and annealed at 80 °C on a hot plate. Although the optimal annealing temperature giving the best electrical conductivity has been reported as 120 °C,²⁵ the films in this

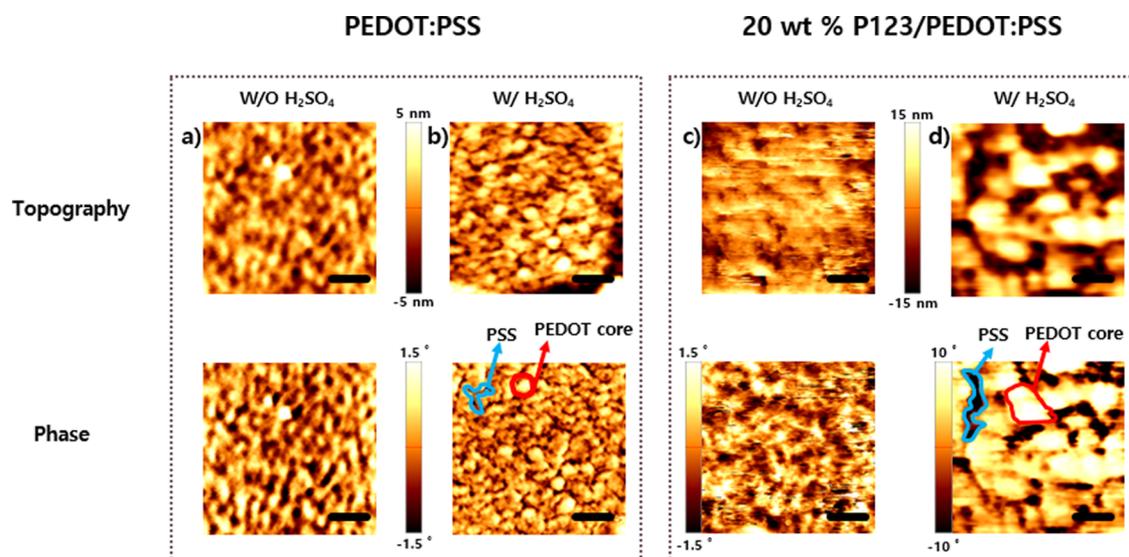


Figure 3. AFM topography and phase images of PEDOT:PSS films: (a) pristine; (b) sulfuric acid-post-treated; (c, d) 20 wt % P123 added to films prepared without and with sulfuric acid post-treatment, respectively. The scale bar is 200 nm.

study were annealed at a relatively low temperature to prevent carbonization of P123 by sulfuric acid residue, which degrades the transmittance and stretchability of PEDOT:PSS film. SEBS was selected as the substrate because its physical properties, including hardness, tensile strength, and elongation, did not significantly change, unlike those of PDMS, when the electrode was post-treated with sulfuric acid. Figure 1b shows the transmittance spectra of a pristine PEDOT:PSS film and 20 wt % P123/PEDOT:PSS films before and after sulfuric acid post-treatment, which had transmittances of 91, 89, and 89% at 550 nm, respectively. All three PEDOT:PSS films showed high transmittance in the visible light range, which is shown in the inset photographical image of Figure 1b.

Figure 2 shows the electrical, electromechanical, and mechanical properties of P123-modified PEDOT:PSS. Figure 2a presents the electrical conductivities of PEDOT:PSS prepared with various P123 concentrations. The conductivity increased with increasing P123 concentration, reaching a peak of ~ 90 S/cm for 5 wt % P123 and decreasing thereafter. When more than 25 wt % P123 was added, the PEDOT:PSS mixture gelled, resulting in a nonuniform spin-coated film. The sheet resistance and thickness used to calculate conductivity of each film are shown in Figure S1. Before sulfuric acid post-treatment, the sheet resistance decreased and the thickness increased by increasing P123 concentration. After sulfuric acid post-treatment, the sheet resistance and thickness largely decreased because sulfuric acid changed the geometry of PEDOT core and dissolved some of P123 out during post-treatment. The change in the normalized resistance (R/R_0) was measured under an applied strain of up to 40% for films with various concentrations of P123. In Figure 2b,c, the 1st stretch–release cycle and the 10th stretch–release cycle after stabilization are presented; we repeated nine stretch–release cycles to stabilize the electrode. The normalized resistances of the 1st and 10th cycles of 1 wt % are shown in Figure S2. Here, R_0 and R represent the resistances measured before and after applying tensile strain, which is defined as follows

$$\text{applied strain (\%)} = \frac{l - l_0}{l_0} \times 100 \quad (2)$$

where l_0 and l are the lengths of the film before and after stretching, respectively. R/R_0 increased 10 times the original when stretched up to 40% for the PEDOT:PSS film prepared with 1 wt % P123. However, for concentration over 5 wt % P123, R/R_0 increased slightly upon stretching; the resistance increases at 40% strain were 8 and 4% for 5, 10, and 20 wt % P123 concentration PEDOT:PSS films. These changes in resistance were much smaller than those previously reported for Zonyl¹⁷ and PEO,³⁰ which showed changes more than 10% at 40% applied strain.

Figure 2d–f shows the electrical characteristics of the films with sulfuric acid post-treatment. The conductivity of PEDOT:PSS dramatically increased after the post-treatment by reconstructing the geometry and size of the PEDOT core (Figure 2d), as previously reported in many studies.^{29,31} The conductivity enhancement mechanism using P123 and sulfuric acid treatment will be discussed in more detail with AFM images in Figure 3. Although the conductivity decreased with the addition of P123, it gradually increased to 1700 S/cm with increasing P123 concentration to 20 wt % after the post-treatment. The resistance changes at the 1st and 10th stretch–release cycles are presented in Figure 2e,f. The normalized resistances of the 1st and 10th cycles of 1 wt % are shown in Figure S2. Resistance change after sulfuric acid post-treatment is increased for 1, 5, and 10 wt %, but in the case of 20 wt % P123/PEDOT:PSS, the R/R_0 versus strain curves were similar regardless of the post-treatment. Therefore, all of the measurements were performed using 20 wt % P123/PEDOT:PSS, which exhibited the smallest change in resistance of about 4% at 40% strain as well as a good electrical conductivity and reproducibility after the sulfuric acid post-treatment. The influences of the sulfuric acid post-treatment time on the electrical conductivity and the change in resistance under applied strain are given in Figure S3. As the treatment time increased, the initial electrical conductivity increased and the resistance change by strain increased greatly. It is due to the formation of irreversible cracks during the stretching deformation. Figure 2g shows the stress–strain curves of free-standing PEDOT:PSS and 20 wt % P123/PEDOT:PSS before and after sulfuric acid post-treatment. In the case of PEDOT:PSS with P123 additives, the tensile strength

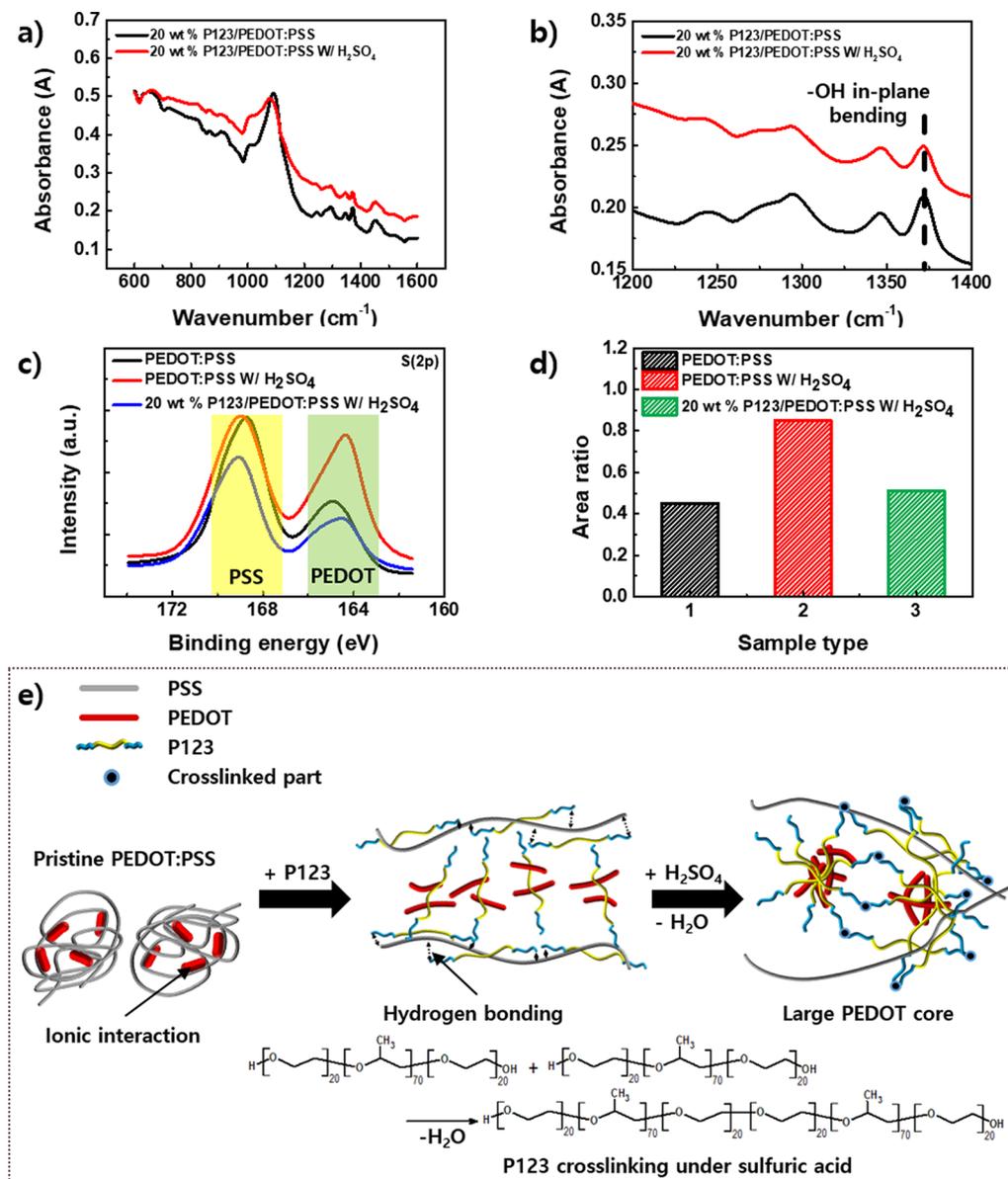


Figure 4. (a) ATR-FTIR of 20 wt % P123/PEDOT:PSS before and after sulfuric acid treatment. (b) Enlargement of ATR-FTIR spectrum near -OH in-plane bending. (c) S 2p XPS images of pristine PEDOT:PSS film and pristine and 20 wt % P123/PEDOT:PSS films prepared with sulfuric acid post-treatment. (d) XPS peak area ratio of PEDOT to PSS. (e) Schematic of possible scenario in the modification of PEDOT:PSS.

decreased from 21.8 to 0.084 MPa and the fracture strain increased from 6.6 to 35.3%, which clearly shows the plasticizing effect of P123. After the post-treatment, the film had the strain limit and tensile strength of 35.7% and 0.119 MPa, respectively. The mechanical analysis proves that P123 improves the stretchability of PEDOT:PSS and that the stretchability of P123/PEDOT:PSS film is maintained even after treatment with sulfuric acid. Young's moduli of the electrodes is summarized in Figure 2h: Young's moduli of pristine PEDOT:PSS and 20 wt % P123/PEDOT:PSS before and after sulfuric acid post-treatment are 765 MPa, 293 kPa, and 384 kPa, respectively.

To understand how P123 and sulfuric acid post-treatment influenced the PEDOT:PSS film surface structure, AFM investigation was carried out. The AFM phase images in Figure 3 show distinctive PEDOT- and PSS-rich grains represented by the bright and dark phases, corresponding to a higher angle and harder materials and a lower angle and softer materials,^{32,33} respectively. Figure 3a,c shows AFM images of pristine

PEDOT:PSS and 20 wt % P123/PEDOT:PSS films, respectively. With the introduction of P123, PEDOT networks became slightly thicker in phase images because of the aggregated PEDOT after separation from PSS.³⁴ Figure 3b,d shows AFM images of sulfuric acid-post-treated PEDOT:PSS films prepared without and with P123, respectively. After the treatment, the PEDOT-rich core became larger and more prominent. To see the effect of the post-treatment with sulfuric acid even without the surfactant, the phase images of Figure 3a,b were simplified into black and white images by using a specialized image processing software ImageJ in Figure S4. The fraction of the PEDOT domain increased from 38.7 to 62.2% approximately after the post-treatment. The size increase in PEDOT core was significant with the P123 additives after post-treatment, as shown in Figure 3d. Large PEDOT cores could improve the electrical conductivity by shortening the current path,^{35,36} while the nonconductive gap between the cores became much larger

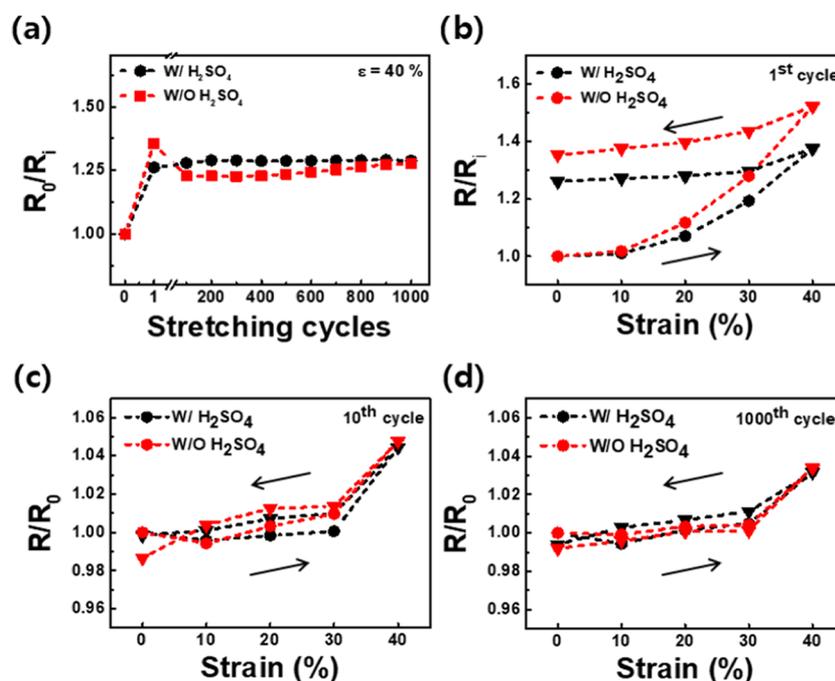


Figure 5. (a) Change of normalized resistance (R_0/R_i) of 20 wt % P123/PEDOT:PSS electrode with repetitive stretch–release cycles under 40% applied strain. Here, R_i and R_0 are the resistances measured before initial stretching and resistance at 0% strain after each cycle, respectively. (b–d) Change in the normalized resistance (R/R_0) with strain at the 1st, 10th, and 1000th stretch cycles, respectively. Here, R and R_0 are the resistances measured with and without applied strain after each cycle, respectively. Circles are for stretching, and reciprocal triangles are for releasing.

than those of the sulfuric acid-treated pristine PEDOT:PSS film, leading to lower electrical conductivity.

To further understand how the P123 and sulfuric acid post-treatment enhanced the electrical conductivity and maintain its stretchability of PEDOT:PSS despite sulfuric acid treatment, ATR-FTIR spectroscopy and XPS images were taken from various PEDOT:PSS films. From the previous research works, P123 can be connected with each other by dehydration cross-linking reaction, which was introduced to synthesize carbon templates.^{37,38} To verify the decrease of the hydroxyl groups of P123, ATR-FTIR spectra were obtained from free-standing P123-modified PEDOT:PSS before and after the post-treatment with sulfuric acid, as shown in Figure 4a,b. The absorption peak at 1372 cm^{-1} , assigned to $-\text{OH}$ in-plane bending,³⁹ decreased in height by 38% from 0.039 to 0.024. Meanwhile, we also checked whether cross-linking between P123 and PSS occur, which was previously reported. However, in Figure S5a, the ATR-FTIR spectrum and its 2nd derivation in $600\text{--}900\text{ cm}^{-1}$ range, corresponding to the $\text{SO}-\text{R}$ bonding,⁴⁰ there was no evidence of new $\text{SO}-\text{R}$ bond. Also, FTIR spectra of free-standing P123 films show similar tendency after the sulfuric acid treatment even in the presence of PSS (Figure S5b).

The chemical compositions of the pristine PEDOT:PSS film and sulfuric acid-treated pristine and 20 wt % P123/PEDOT:PSS films were investigated by XPS analysis, as shown in Figure 4c. The ratios of PEDOT to PSS were calculated using the ratios of peak areas in the ranges of 163–166 and 167–172 eV, corresponding to PEDOT thiophene rings and PSS sulfonate groups, respectively.⁴¹ Figure 4d shows that the ratio of PEDOT to PSS increased from 0.45 to 0.8 when PEDOT:PSS film was treated with sulfuric acid because PSS was dissolved out of the film during the wash out of sulfuric acid with DI water.²⁵ The high PEDOT ratio implies that the conductive PEDOT cores were well interconnected without interfering with

the nonconductive gap,⁴² leading to higher conductivity, as seen in Figure 2d. The ratio of PEDOT to PSS estimated from the sulfuric acid-treated 20 wt % P123/PEDOT:PSS film was 0.51. This might have been caused by the cross-linking of P123, which prohibits PSS from being dissolved. The XPS images of the films showed that the dissolution of PSS was not critical in enhancing the conductivity of the P123/PEDOT:PSS film. In Figure S6, fitting of the XPS data for each film is given.

To explain the experimental results, we propose a possible scenario in Figure 4e. The electrical conductivity of PEDOT:PSS film seems to be improved in two steps: first, the addition of P123 separates PEDOT and PSS. The ionic interaction between PEDOT and PSS is weakened due to the hydroxyl group of P123, which forms hydrogen bonding with PSS, similar to other additives that have hydroxyl group, such as PEO.^{4,31} The separated PEDOT chains are aggregated by P123, as evidenced by the AFM images in Figure 3.³⁴ Subsequently, the large PEDOT core can be formed, presumably by dehydration via cross-linking of P123. By introducing the two factors in PEDOT:PSS modifications, the conductivity and stretchability can be enhanced compared to the pristine PEDOT:PSS film.

The 20 wt % P123/PEDOT:PSS electrode demonstrated excellent durability and reliability upon stretching deformation regardless of the post-treatment with sulfuric acid in Figure 5. After the initial stretch by 40%, the resistances of the electrodes fabricated with and without sulfuric acid post-treatment increased by 25 and 35%, respectively. In Figure 5a, R_i and R_0 are the resistance measured before initial stretching and resistance at 0% strain after each cycle, respectively. After the initial stretch cycle, R_0 of the post-treated electrode remained almost the same during 1000 stretch–release cycles under the same applied strain of 40% for both electrodes. Figure 5b–d shows the change in normalized resistance under varying applied

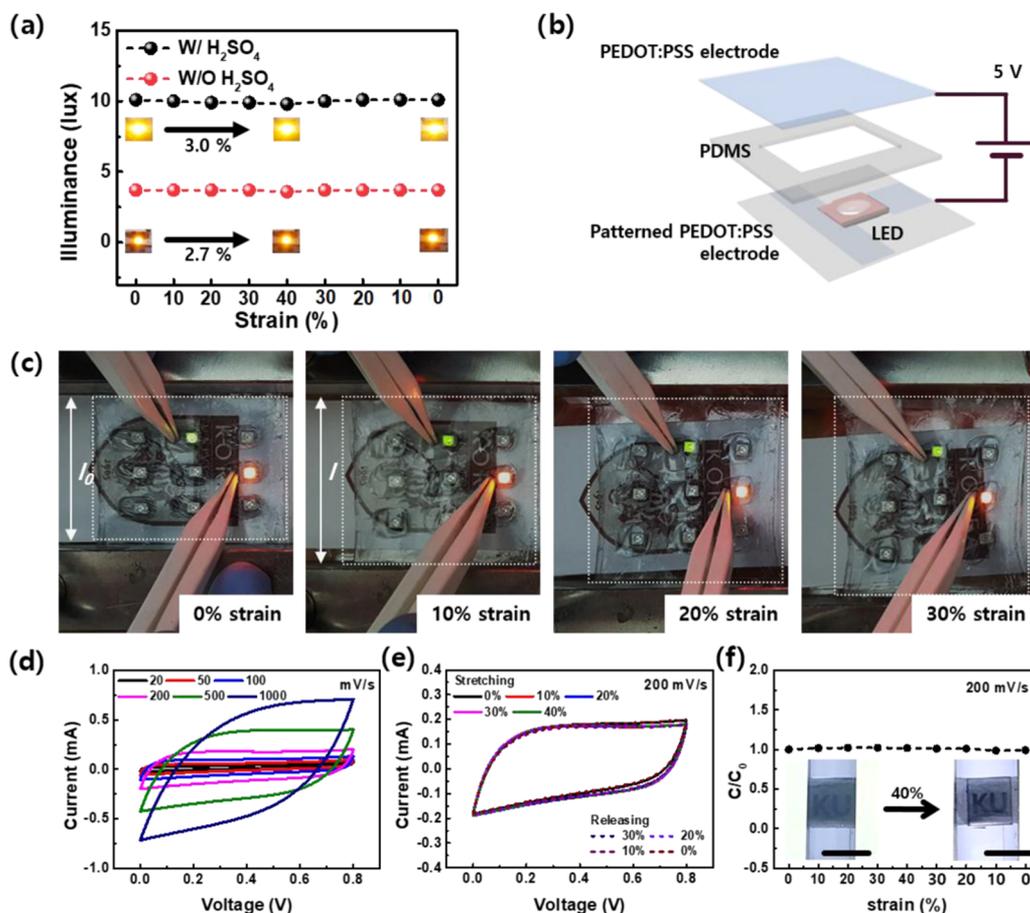


Figure 6. (a) Brightness of LED under applied strain onto the electrodes fabricated with (black) and without (red) sulfuric acid post-treatment. The insets show photographs of lit LED. (b) Schematic of switch-type stretchable transparent touch sensor. (c) Optical images of the touch sensor under applied strain up to 30%. Here, l_0 and l are the lengths of the touch sensor before and after stretching, respectively, as marked in images. (d) CV curves of the supercapacitor with variation of scan rates. (e) CV curves under uniaxial stretching up to 40%. (f) Normalized capacitance with stretch–release cycle. The insets show the semitransparency of the supercapacitor (scale bar = 1 cm).

strains during the 1st, 10th, and 1000th stretch cycles, respectively. Both films exhibited only small increases in resistance during stretching, $\sim 4\%$ at an applied strain of 40%, further demonstrating the mechanical stability of our transparent electrodes. Previous studies have suggested that size increase of the PEDOT core during stretching suppresses the increase of resistance according to the tensile strain.^{35,43} The absolute resistance values of the electrodes are shown in Figure S7.

Figure 6 shows the demonstration of the fabricated PEDOT:PSS films as stretchable, transparent, and conductive electrodes. Figure 6a shows negligible changes in brightness with values slightly decreased by 3.0 and 2.7% for the films treated with and without sulfuric acid, respectively, at 40% strain. When the film was post-treated with sulfuric acid, much higher brightness of the LED was observed for the same applied voltage of 3 V. We also fabricated a 3×3 array of switch-type stretchable touch sensors, which were integrated with nine LEDs, as shown in Figure 6b. LEDs were lit up upon touching the corresponding sensor areas, consisting of the top and bottom electrodes with sulfuric acid-post-treated 20 wt % P123/PEDOT:PSS. When the top electrode is pressed, contact is made with the bottom electrode. Therefore, current flows to turn on each corresponding LED. In Figure 6c, there was no notable degradation of the brightness of the lit LEDs even under uniaxial stretching up to 30% of the applied strain. These results clearly demonstrate the

high potentials of the fabricated stretchable, transparent, and conductive electrodes in application to stretchable electronics, including sensors and interconnections.

We also fabricated a stretchable semitransparent supercapacitor as another application. The supercapacitor has a simple structure with an PVA/H₃PO₄ electrolyte stacked between two CNT-coated PEDOT:PSS electrodes. Here, CNTs were used for increasing capacitance. The schematic structure of the supercapacitor is presented in Figure S8. Cyclic voltammetry (CV) and charge–discharge curves measured with various scan rates are presented in Figures 6d and S8, which reveal the stable electrochemical performance of the supercapacitor. Even under stretching up to 40% strain, the electrochemical performance and the capacitance were unchanged, as shown in Figure 6e,f. The capacitance was calculated based on the CV curves in Figure 6e.

4. CONCLUSIONS

We report the facile fabrication of highly conductive, stretchable, and transparent PEDOT:PSS electrodes achieved by modification with P123 and sulfuric acid. The electrodes exhibited only $\sim 4\%$ change in resistance over 1000 stretch–release cycles under applied strains up to 40% as well as high transparency ($\sim 89\%$) and high initial electrical conductivity (~ 1700 S/cm). Through systematic analyses, the underlying two-step mecha-

nism for the enhanced electrical conductivity and stretchability was suggested in terms of the separation of PEDOT and PSS by P123 and the subsequent increase in the size of the conductive PEDOT core via aggregation of PDEOT due to modification with P123 and sulfuric acid. Furthermore, our electrodes showed a high potential in the application to stretchable electronics by demonstrating mechanically stable LED circuits, touch sensor arrays, and supercapacitor under stretching deformation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b07287.

Sheet resistance and thickness of P123/PEDOT:PSS with various P123 concentrations; normalized resistance of P123/PEDOT:PSS with various P123 concentrations before and after sulfuric acid post-treatment for increasing number of stretch cycles; conductivity and normalized resistance of the 1st cycle of 20 wt % P123/PEDOT:PSS depending on sulfuric acid post-treatment time; AFM phase image of pristine PEDOT:PSS before and after sulfuric post-treatment; ATR-FTIR spectrum of 20 wt % p123/PEDOT:PSS before and after sulfuric acid post-treatment and its 2nd derivative; ATR-FTIR spectra of P123 and P123/PSS complex before and after sulfuric acid post-treatment; S 2p XPS images of pristine PEDOT:PSS, PEDOT:PSS treated with sulfuric acid, and 20 wt % P123/PEDOT:PSS treated with sulfuric acid; absolute resistance of the electrode during stretching; and schematic of stretchable semitransparent supercapacitor and charge–discharge curve of the supercapacitor (PDF)

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Notes

The authors declare no competing financial interest.

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