

**Synthesis of Poly(3,4-ethylenedioxythiophene)–Platinum and Poly(3,4-ethylenedioxythiophene)–Poly(styrenesulfonate) Hybrid Fibers by Alternating Current Bipolar Electropolymerization**

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## ***Experimental Section***

### **Materials**

3,4-Ethylenedioxythiophene (EDOT), hexachloroplatinic(IV) acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), and anhydrous acetonitrile (MeCN) were purchased from Wako. Silver(I) tetrafluoroborate ( $\text{AgBF}_4$ ) was purchased from Merck. Poly(sodium 4-styrenesulfonate) (PSSNa, average  $M_w \sim 70,000$ , 30 wt. % in  $\text{H}_2\text{O}$ ) was purchased from Aldrich. Sodium *p*-toluenesulfonate (TsNa) was purchased from TCI. All reagents and dry acetonitrile were used without further purification. All aqueous solutions were prepared with deionized water. Electrolytic solutions were deaerated by an intensive Ar bubbling just before use. Gold wires, platinum plates and glassy carbon plates were purchased from Nilaco.

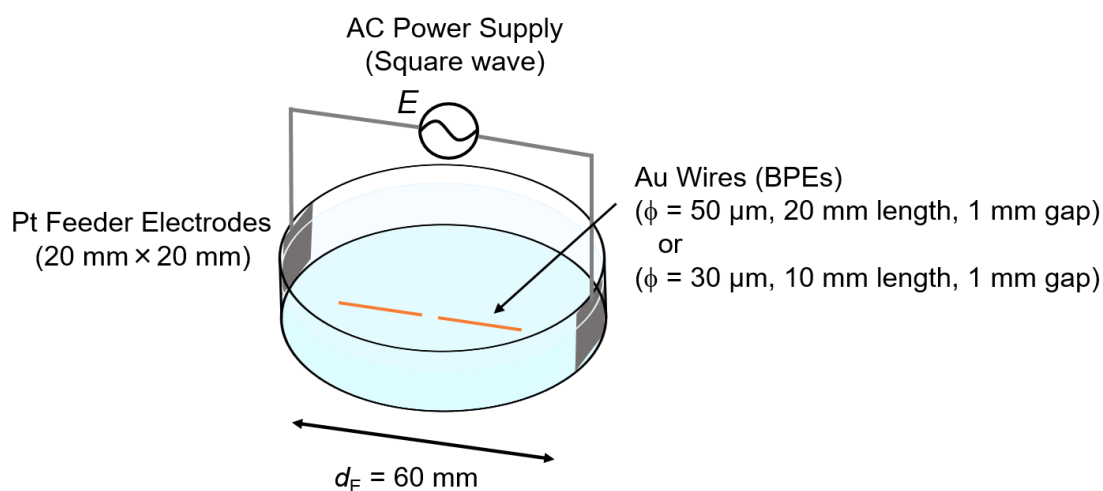
### **Instruments**

Alternating current (AC) power was supplied to the feeder electrodes using an EC1000SA AC/DC power source (NF Corporation). Optical microscope observations were conducted with an Olympus SZX10, and scanning electron microscopy (SEM) observation was performed using a Shimadzu SS-550. Field Emission-Scanning Electron Microscopy (FE-SEM) observation was performed using a Hitachi High-Technologies S-5500. Transmission Electron Microscopy (TEM) observation were performed using a JEOL JEM-2100. Energy dispersive X-ray (EDX) spectra were acquired with a JEOL JED-2300T. Cyclic voltammetry (CV) measurements were carried out using an ALS 6005C Electrochemical Analyzer. Conductivity measurements were performed by using Mitsubishi

Chemical Analytech Loresta-GX MPC-T700. Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed using a Shimadzu IR Tracer-100. Thermogravimetric analysis was carried out using Shimadzu DTG-60.

### Cell Configuration

The glass cell equipped with Pt feeder electrodes (20 mm × 20 mm, distance: 60 mm) was filled with an electrolytic solution. Two Au wires were placed 1 mm apart from one another between the feeder electrodes (Figure S1).



**Figure S1.** Illustration of an electrolytic cell for AC-bipolar electropolymerization.

### Estimation of $\Delta V_{\text{BPE}}$

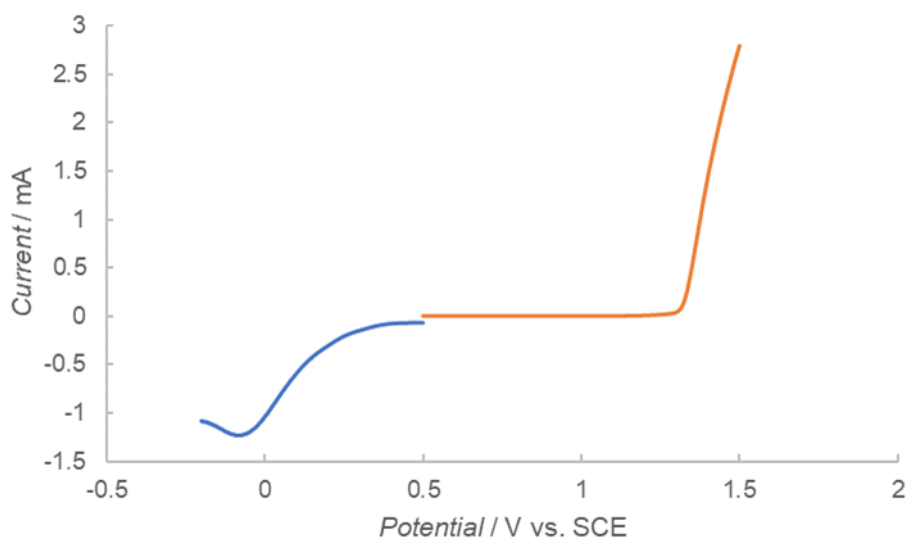
The minimum applied voltage required to induce BPE ( $\Delta V_{\text{min}}$ ) was estimated from the difference between the oxidation and reduction potentials of the corresponding species,  $E_{\text{ox}}$  and  $E_{\text{red}}$ , (Eq. 1), as previously reported.<sup>1</sup>

$$\Delta V_{\min} = |E_{\text{ox}} - E_{\text{red}}| \quad (1)$$

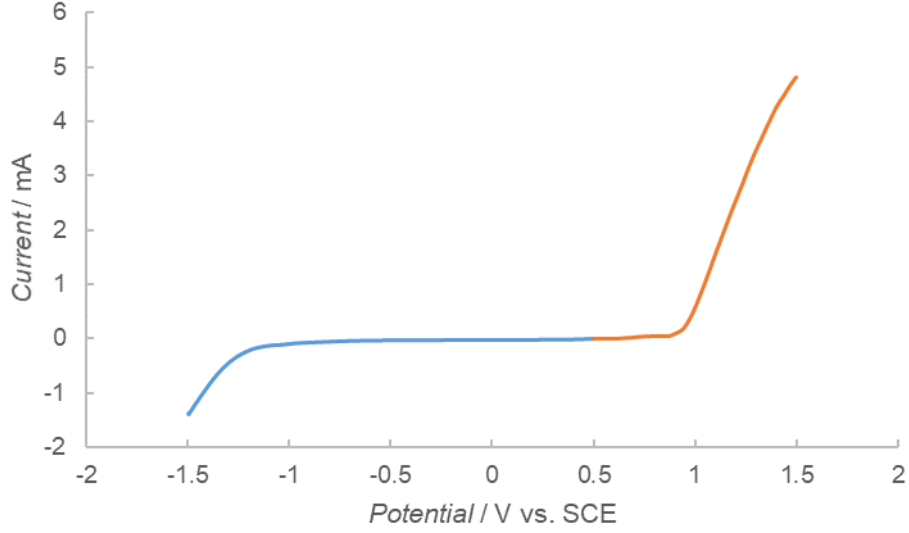
In this system, the oxidation of EDOT and the reduction of  $[\text{PtCl}_6]^{2-}$  or  $\text{H}_2\text{O}$  were assumed to occur simultaneously on the BPE. Using the onset potentials of these half reactions (Figures S1 and S2),  $\Delta V_{\min}$  was estimated using Eq. 2 or Eq. 3.

$$\Delta V_{\min} = |E_{\text{ox}} - E_{\text{red}}| = |1.33 \text{ V} - (0.24 \text{ V})| = 1.09 \text{ V} \quad (2)$$

$$\Delta V_{\min} = |E_{\text{ox}} - E_{\text{red}}| = |1.33 \text{ V} - (-0.02 \text{ V})| = 1.35 \text{ V} \quad (3)$$



**Figure S2.** Linear sweep voltammograms of EDOT (10 mM) and  $\text{H}_2\text{PtCl}_6$  (10 mM) measured independently in 0.1 M  $\text{Bu}_4\text{NClO}_4/\text{MeCN}$  using ITO working electrode (10 mm  $\times$  10 mm) at a scan rate of 100 mV/s.



**Figure S3.** Linear sweep voltammograms of EDOT (10 mM) in 0.1 M TsNa/H<sub>2</sub>O using ITO working electrode (10 mm × 10 mm) at a scan rate of 100 mV/s.

#### Estimation of Cell Factors and $\Delta V_{\text{BPE}}$

In order to estimate a cell factor, i.e., the electric field transmission efficiency  $\theta$ , a ratio of electric field inside the cell ( $\varepsilon_{\text{eff}}$ ) and applied electric field between driving electrodes ( $\varepsilon$ ) is defined as follows.<sup>1-4</sup>

$$\theta = \frac{\varepsilon_{\text{eff}}}{\varepsilon} \quad (4)$$

It follows that

$$\theta = \frac{U_m d_E}{d_m E} \quad (5)$$

and

$$U_m = \theta \frac{d_m E}{d_E} \quad (6)$$

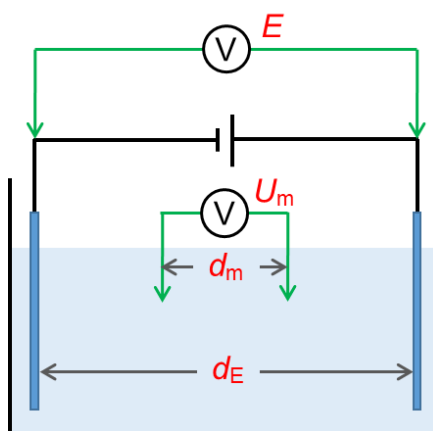
where  $U_m$  is the potential difference measured between two microelectrodes with distance of  $d_m$ ,  $E$  is the applied voltage between the driving electrodes set with distance of  $d_E$  (Figure S3). Based on Eq.

6, a value of  $\theta$  can be estimated from slope of plots of  $U_m$  as a function of  $Ed_m/d_E$ ; thus, a potential

applied between each bipolar electrode ( $\Delta V_{BPE}$ ) can be estimated as follows:

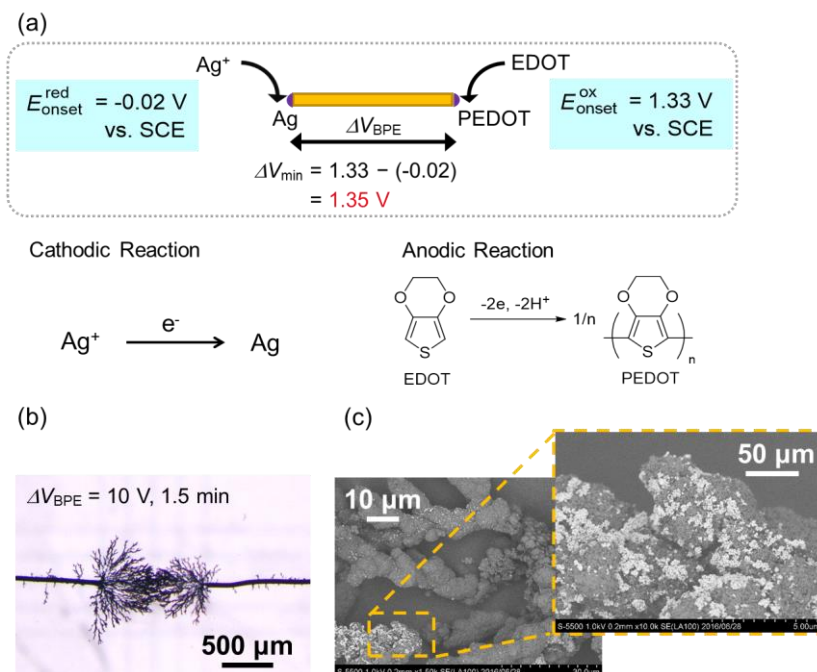
$$\Delta V_{BPE} = \theta \frac{d_{BPE} E}{d_E} \quad (7)$$

where  $d_{BPE}$  is the length of bipolar electrode. The value of  $\Delta V_{BPE}$  was stable for the time scale of the electrolysis.



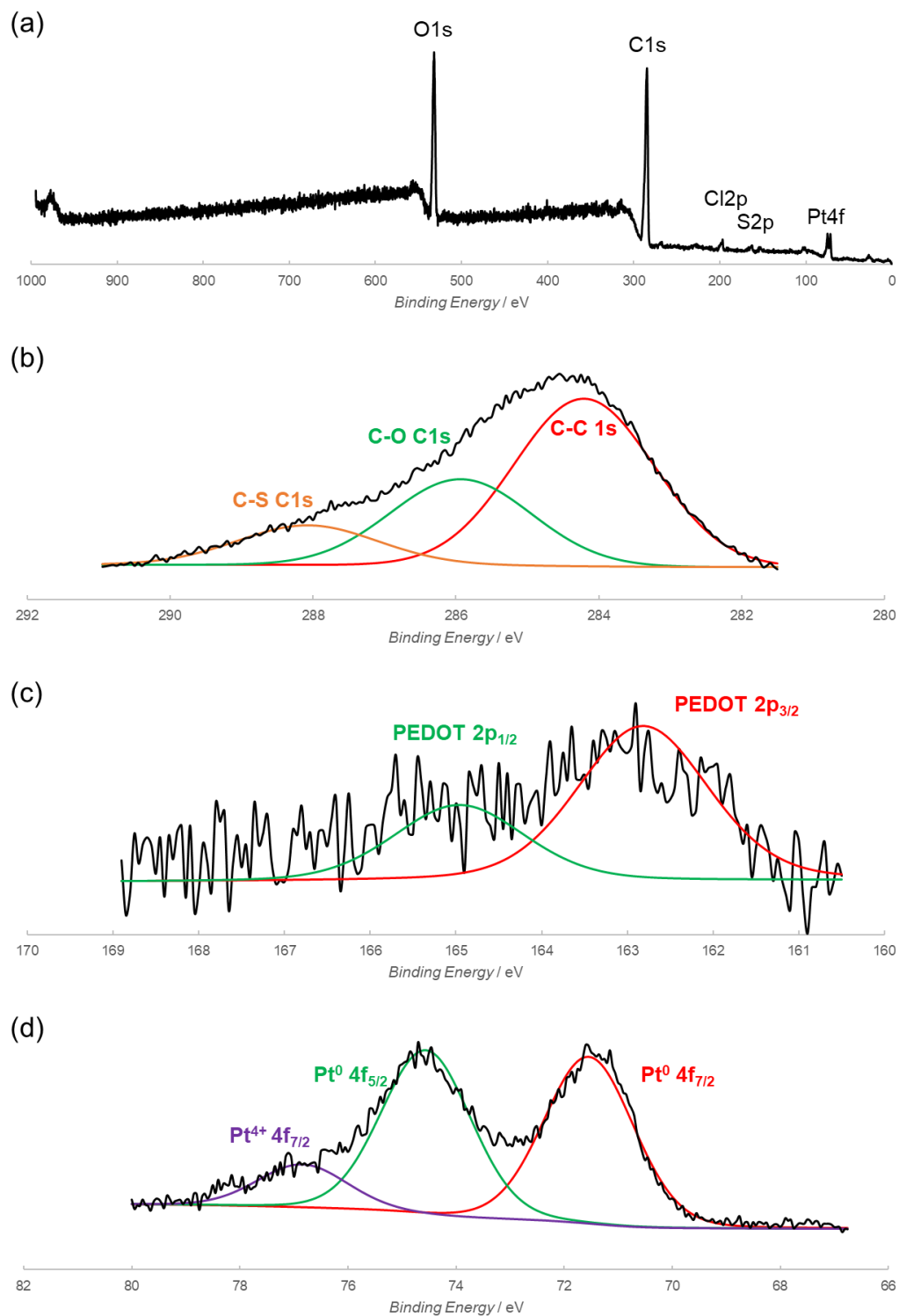
**Figure S4.** Cell configuration and definition of the parameters for the equations.

## AC-bipolar Electropolymerization for Synthesis of PEDOT–Ag Hybrid Fibers



**Figure S5.** (a) Schematic illustration of the electrochemical reactions in the AC-bipolar electrolysis, including oxidative polymerization of EDOT and sacrificial reduction of  $\text{Ag}^+$  with Au wires as BPEs set in between feeder Pt electrodes, (b) optical microscope image of PEDOT–Ag hybrid fibers bridging the 1 mm gap between Au wires ( $\Delta V_{\text{BPE}} = 10 \text{ V, 1.5 min, 5 Hz}$ ), and (c) FE-SEM images of the PEDOT–Ag hybrid fibers.

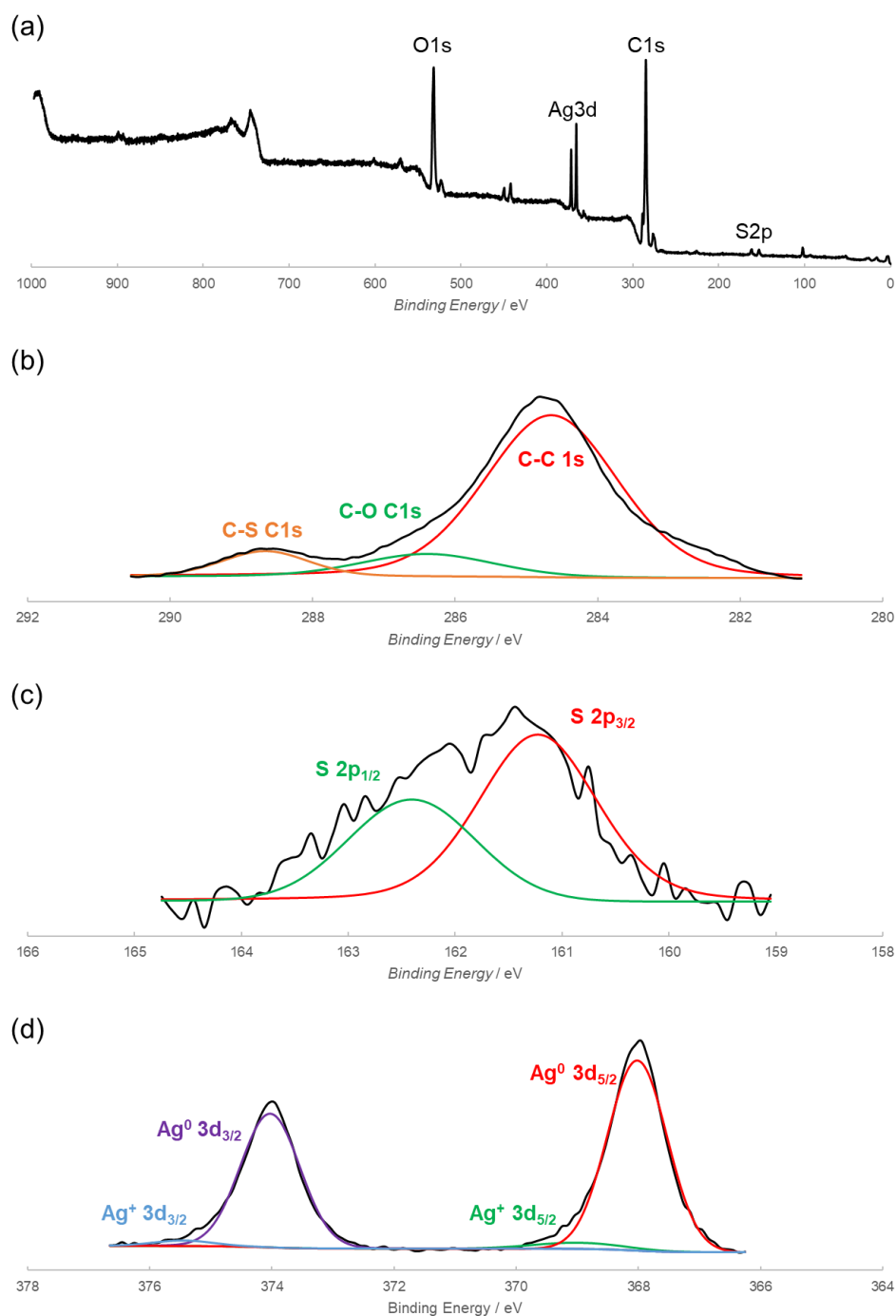
## XPS Spectra of PEDOT–Pt Hybrid Fibers



**Figure S6.** (a) XPS survey spectra for PEDOT–Pt hybrid fibers. (b,c,d) Deconvoluted C1s, S2p and Pt4f XPS spectrum for PEDOT–Pt hybrid fibers.



## XPS Spectra of PEDOT–Ag Hybrid Fibers

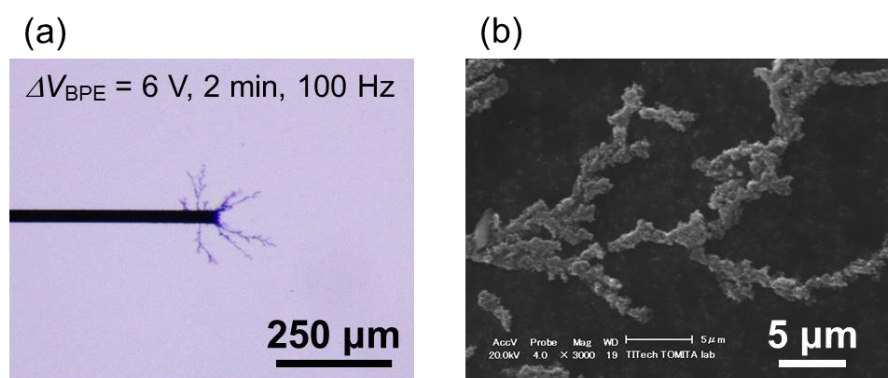


**Figure S7.** (a) XPS survey spectra for PEDOT–Ag hybrid fibers. (b,c,d) Deconvoluted C1s, S2p, Ag3d XPS spectrum for PEDOT–Ag hybrid fibers.

## Cyclic Voltammetry Measurements for PEDOT Fibers and PEDOT–Pt Hybrid Fibers

The working electrode for CV measurements was prepared by encapsulating the PEDOT fibers or the PEDOT–Pt hybrid fibers in a non-conducting sheath of epoxy resin onto a well-polished glassy carbon plate. The exposed fibers were in the forms of rectangle with the areas of  $1\text{ mm} \times 2\text{ mm}$ . The glassy carbon plate electrode was connected to a lead wire by spot welding, and the wire part was encapsulated in a non-conducting sheath of glass. The CV measurement for each fiber was conducted in  $0.1\text{ M H}_2\text{SO}_4/\text{H}_2\text{O}$  in the potential range from  $-0.3\text{ V vs. SCE}$  to  $+1.0\text{ V vs. SCE}$  at a scan rate of  $100\text{ mVs}^{-1}$ .

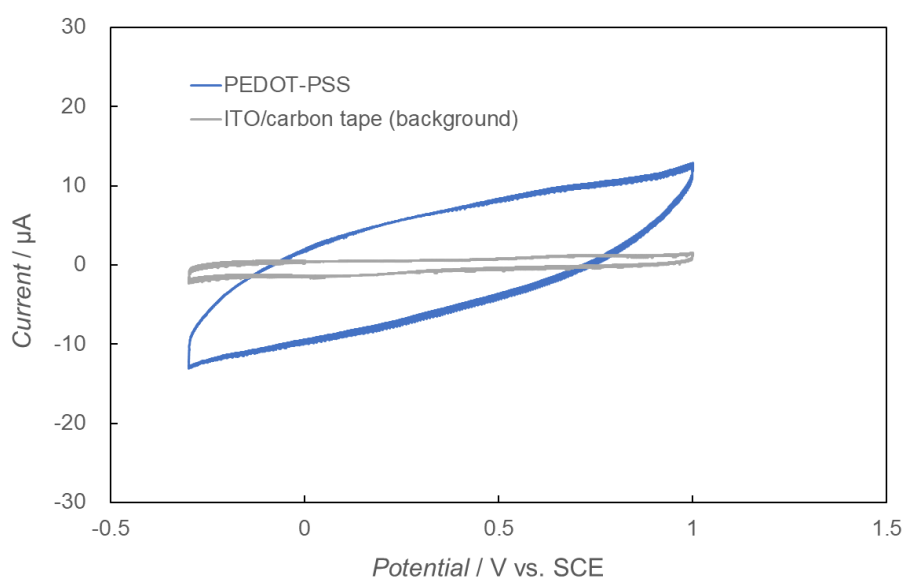
## AC-bipolar Electropolymerization for Synthesis of PEDOT–Ts Hybrid Fibers



**Figure S8.** (a) Optical microscope image of PEDOT–Ts hybrid fibers grown from Au wires ( $\Delta V_{\text{BPE}} = 7\text{ V}$ ,  $1.5\text{ min}$ ,  $5\text{ Hz}$ ), and (b) SEM images of the PEDOT–Ts hybrid fibers.

## Cyclic Voltammetry Measurements for PEDOT–PSS Hybrid Fibers

A small piece of PEDOT–PSS hybrid fiber was transferred onto a carbon tape (5 mm × 10 mm) fixed on an ITO electrode (10 mm × 10 mm), which was used as a working electrode. The CV measurement for the fiber was conducted in 0.1 M H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O in the range from –0.3 V vs. SCE to +1.0 V vs. SCE at a scan rate of 100 mVs<sup>–1</sup>.



**Figure S9.** Cyclic voltammograms of PEDOT–PSS fibers (blue line) and background (gray line) on a carbon tape fixed on an ITO electrode, measured in 0.1 M H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O at a scan rate of 100 mV/s.

## References

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- (2) Koizumi, Y.; Shida, N.; Tomita, I.; Inagi, S. Bifunctional Modification of Conductive Particles by Iterative Bipolar Electrodeposition of Metals. *Chem. Lett.* **2014**, *43*, 1245–1247.
- (3) Koizumi, Y.; Masato, O.; Nishiyama, H.; Tomita, I.; Inagi, S. Electropolymerization on Wireless Electrodes towards Conducting Polymer Microfibre Networks. *Nat. Commun.* **2016**, *7*, 10404.
- (4) Ohira, M.; Koizumi, Y.; Nishiyama, H.; Tomita, I.; Inagi, S. Synthesis of Linear PEDOT Fibers by AC-Bipolar Electropolymerization in a Micro Space. *Polym. J.* **2017**, *49*, 163–167.