Electronic Supplementary Information

Aligned Carbon and Graphite Fibers Prepared from Poly(3,4-ethylenedioxythiophene) Single Crystals Synthesized by Solid-State Polymerization and Their Supercapacitor Performance

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Materials and Measurements

1. Materials. The chemical compounds were purchased from commercially available sources and were used as received.   The compound, acetic acid (CH_3COOH), sodium hydrogen carbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), hydrazine monohydrate, and sodium hydroxide ($NaOH$) were purchased from Nacalai Tesque, Inc.   The compound, *N*-bromosuccinimide (NBS) and 3,4-ethylenedioxythiophene (EDOT) were purchased from Tokyo Chemical Industry Co., Ltd.   Aluminum powder was purchased from Nilaco Co., Ltd.   Carbon black (Super P, conductive, 99+ %) was purchased from Alfa Aesar.   Polytetrafluoroethylene preparation (60 wt %, dispersion in H_2O) was purchased from Aldrich.   Kish graphite powder was purchased from commercially available source. Acetone, acetonitrile (ACN), ethanol (EtOH), and chloroform ($CHCl_3$) (Nacalai Tesque, Inc.) were used as received.   EDOT was distilled under reduced pressure in argon gas atmosphere before use (b.p. = ~200 °C/760 mmHg, 112 °C/20 mmHg).   Nickel foam was purchased from MTI Corporation. Platinum (Pt) wire counter electrode was purchased from Metrohm Autolab.   RE-61AP reference electrode for alkaline solution was purchased from BAS, Inc.

2. Measurements. Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-d using a JEOL EX-400 and an AL-400 NMR spectrometer.   Chemical shifts are represented in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard.   Elemental analysis was performed at the Center for Organic Elemental Microanalysis of Kyoto University.   The molecular ratio of doped bromine ion (Br^-) to EDOT unit in the PEDOT fiber (Br^-/EDOT) was calculated from the elemental analysis.   The sum of all the elements is assumed to be 100%.   High-resolution mass spectra (HRMS) were obtained by using Thermo Fisher Scientific EXACTIVE (ACPI).

Thermal behavior of PEDOTs was investigated in a heating run at a heating rate of 10 °C/min in flowing nitrogen gas, using thermogravimetry-differential thermal analysis (TG-DTA) apparatus (DTG-60, Shimadzu) with alumina pan.　Before the TG-DTA measurements, the PEDOT fibers were dried through vacuum pumping for several hours.

The fiber thickness was measured using Nikon Digimicro digital length measuring system with DIGIMICRO MH-15M, DIGIMICRO STAND MS-5C, and DIGITAL READOUT UC-101.

The electrical conductivity of the graphite fiber was measured at room temperature using a low resistivity meter, Loresta GP with a MCP-TP06P probe (Mitsubishi Chemical Analytech).

X-ray diffraction (XRD) measurements were performed with a Rigaku ultra X18 diffractometer. XRD patterns were recorded with an X-ray generator with Ni filtered CuKα radiation (40 kV/300 mA: λ = 1.54 Å) and a flat-plate camera (RINT2500, Rigaku).　The sample-to-film distance was 100 mm calibrated using a (111) face of aluminum (d = 2.33787 Å) and exposure time was 1–2 h.　The diffraction pattern was recorded on an imaging plate and scanned by a RAXIA-Di imaging plate reader at 100 μm resolution.　The crystal size along the c-axis (L_c) of the graphite film was estimated from the (002) diffraction peak of the XRD pattern by means of the Scherrer equation, $L = K\lambda/\beta\cos\theta$, where K is the shape factor and adopted to be 0.94, λ is the X-ray wavelength, β is the peak width at half maximum in radians, and θ is the Bragg angle.[1]　The degree of orientation of the graphite fiber was estimated using Hermans' (second-order) orientation factor (f) based on the (110) and (200) reflections of the pattern using the equation $f = (\langle 3\cos^2 \varphi \rangle - 1)/2$, where φ is the peak width at half-maximum for the azimuthal-angle profile.[2]

Raman spectra were obtained at room temperature by backscattering method, using a spectroscope with a triple monochromator and a charge-coupled device (CCD) detector cooled by Peltier device (NRS-2100 or NRS-4100, JASCO).　A 100 mW argon ion laser with a wavelength of 514.5 nm was

used.   An exposure time was 40 sec (10 sec × 4).   The crystal sizes along the a-axis (L_a) of the carbon and graphite fibers were estimated from the Raman spectra by means of the equation, $L_a = 4.35(I'_D/I'_G)^{-1}$, where I'_D and I'_G are integrated intensities of the D-band and G-band, respectively.[3,4] I'_D and I'_G are peak intensities of the D-band and G-band, respectively.   The Raman spectra were fitted with a mixed Gaussian-Lorentzian function using the software PeakFit®.

Ultraviolet−visible−NIR (UV−vis−NIR) spectrum was measured using JASCO V570.

Infrared (IR) absorption spectra of PEDOT fibers were measured in powdery solid state with a JASCO FT (Fourier transform)-IR 4200 spectrometer using transmission mode, KBr method.

The accelerating voltage of field emission (FE)-SEM (JSM-7500F, JEOL) was 2−10 kV.   The DBEDOT and SSP-PEDOT fibers were coated with Pt or Pt-Pd alloy using an ion coater with type of JFC-1600 (JEOL) before measurements of SEM.   The coating thickness was evaluated to be ca. 5 nm.

The carbon fibers were prepared by using an electric furnace (KDF75, Denken).   The graphite fibers were prepared by using a graphitization apparatus [SCC-U-80/150 (2P), Kurata-giken].

Carbonization and graphitization yields were evaluated using the equations, (weight of carbonized PEDOT)/(weight of PEDOT)×100 and (weight of graphitized fiber)/(weight of carbon fiber)×100, respectively.

Spin coater (Opticoat MS-A150, MIKASA Corp.) was used for preparing DBEDOT monomer films on glass substrates.

Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were performed with μAUTOLAB III potentiostat/galvanostat.

The specific capacitance values calculated from CV (C_v) results are based on equation

$$C_v = \int_{E_1}^{E_2} i(E)dE/2(E_2 - E_1 mv)$$,

where $\int_{E_1}^{E_2} i(E)dE$ is the total voltammetric charge obtained by integration of positive and negative sweep,

E_1 and E_2 are potential limits, m is the mass of sample, and v is the scan rate.

The specific capacitance values calculated from GCD (C_m) results are based on equation

$$C_m = \frac{C}{m} = \frac{I \times \Delta t}{\Delta V \times m}$$,

where the I is discharge current, Δt is the discharging time, ΔV is the potential drop during the discharge

process in the range of V_{max} and V_{min}, and m is the mass of the sample.

Synthesis

2,5-Dibromo-3,4-ethylenedioxythiophene (DBEDOT)
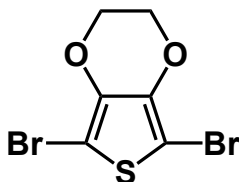
To a stirred solution of EDOT (3.0 g, 21.1 mmol) dissolved in 2 : 1 solvent mixture of distilled CHCl$_3$ (60 mL) and acetic acid (30 mL) was added by slowly NBS (9.38 g, 52.7 mmol) under argon atmosphere.   The mixture was allowed to stir for 4 h at room temperature and quenched with water. The organic layer was separated, and the water layer was extracted with CHCl$_3$ (×3).   The combine CHCl$_3$ extract was neutralized with NaHCO$_3$ solution, washed with distilled water, and dried with anhydrous sodium sulfate.   The filtered solution was passed through a dry flash silica column using CHCl$_3$ as the eluent.   The crude product was further purified by recrystallization in EtOH affording a white crystalline solid with yield of 55% (3.5 g).   Anal., calcd for C$_6$H$_4$Br$_2$O$_2$S: C, 24.02; H, 1.34; Br, 53.28; O, 10.67; S, 10.69.   Found: C, 24.15; H, 1.33; Br, 52.15; S, 10.70.   MS (APCI) calcd for C$_6$H$_4$Br$_2$O$_2$S [M+H$^+$]: 298.84.   Found: 298.84. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.27 (s, 4H, −OCH_2). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 64.9, 84.6, 140.1.

## 5,5'-Dibromo-2,2'-bis(3,4-ethylenedioxythiophene) [DB*bis*EDOT]
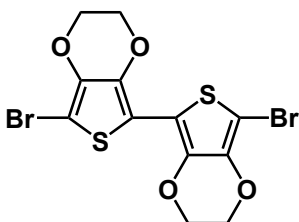
To a stirred solution of 2,2'-bis(3,4-ethylenedioxythiophene) (*Bis*-EDOT) (1.5 g, 5.3 mmol) dissolved in 2 : 1 solvent mixture of distilled CHCl$_3$ (30 mL) and acetic acid (15 mL) was added by slowly NBS

(2.4 g, 13.3 mmol) in the dark at 0 °C under argon atmosphere.   The mixture was allowed to stir for 4 h at 0 °C and quenched with water.   The organic layer was separated, and the water layer was extracted with CHCl$_3$ (×3).   The combine CHCl$_3$ extract was neutralized with NaHCO$_3$ solution, washed with distilled water, and dried with anhydrous sodium sulfate.   The filtered solution was passed through a dry flash silica column using CHCl$_3$ as the eluent.   The crude product was further purified by recrystallization in EtOH affording a yellow solid with yield of 51% (1.2 g).   Anal., calcd for C$_{12}$H$_8$Br$_2$O$_4$S: C, 32.75; H, 1.83; Br, 36.31; O, 14.54; S, 14.57.   Found: C, 32.65; H, 1.86; Br, 35.53; S, 14.59.   MS (APCI) calcd for C$_{12}$H$_8$Br$_2$O$_4$S [M+H$^+$]: 438.83.   Found: 438.83. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.28 (s, 8H, −OCH$_2$).

Supporting References

1 J. Biscoe, B. E. Warren, *J. Appl. Phys.*, 1942, **13**, 364−371.

2 P. H. Hermans, P. Platzek, *Kolloid-Z.*, 1939, **88**, 68−72.

3 F. Tuinstra, J. L. Koenig, *J. Chem. Phys.*, 1970, **53**, 1126−1130.

4 D. S. W. Knight, B. White, *J. Mater. Res.*, 1989, **4**, 385−393.

5 S. Matsushita, B. Yan, S. Yamamoto, Y. S. Jeong, K. Akagi, *Angew. Chem., Int. Ed.*, 2014, **53**, 1659−1663.

Supporting Figures
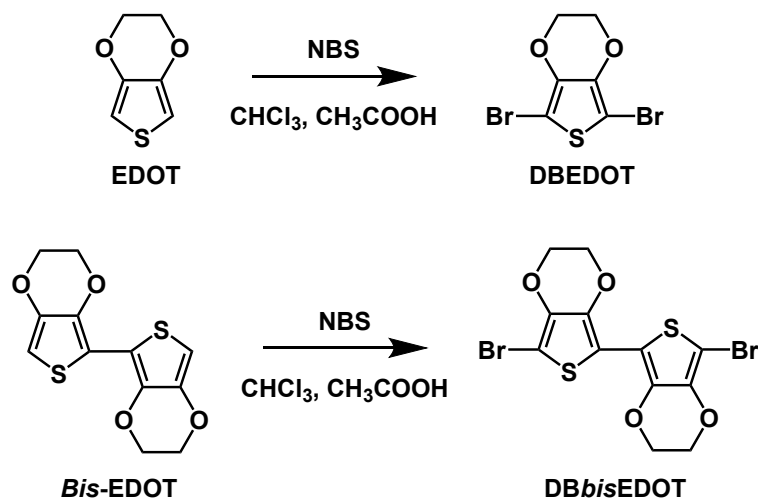
Scheme S1. Synthetic routes of DBEDOT and DB*bis*EDOT.
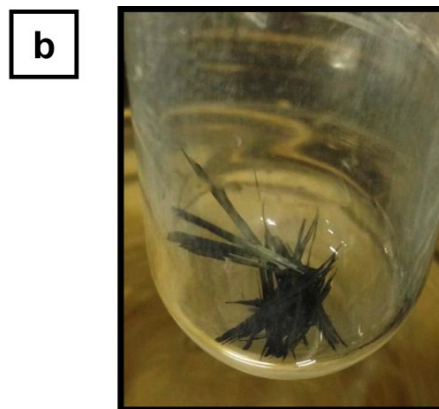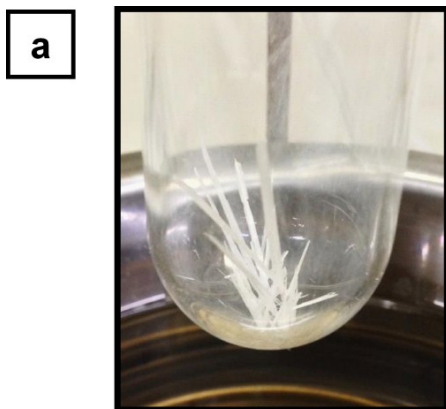
Fig. S1 Photographs of the (a) DBEDOT and (b) SSP-PEDOT fibers.
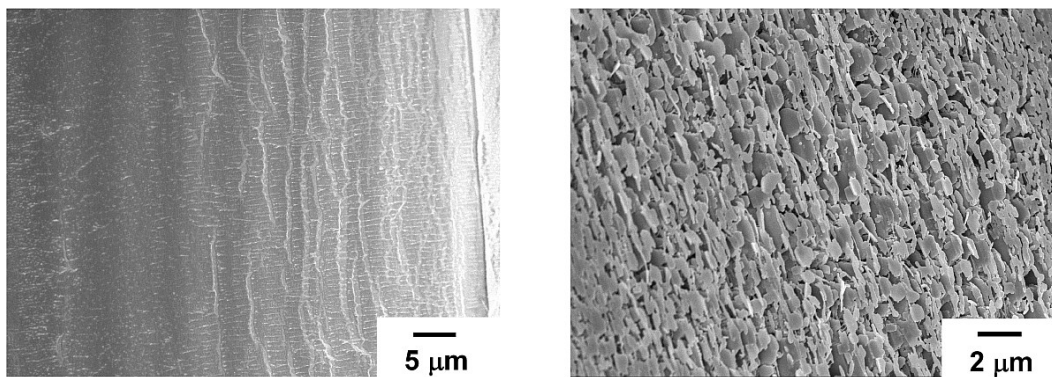
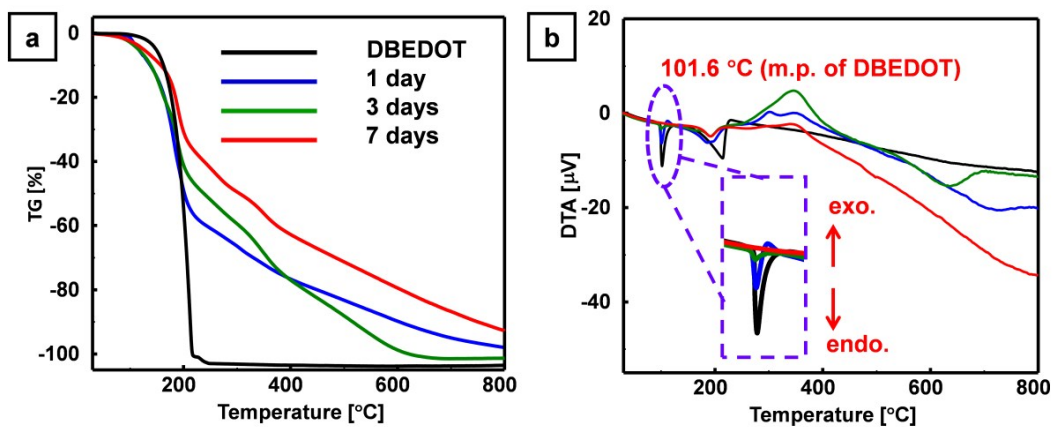**Fig. S2** SEM images of the DBEDOT (left) and doped SSP-PEDOT (right) fibers.

Fig. S3 (a) TG and (b) DTA curves of DBEDOT and doped SSP-PEDOT fibers with various polymerization time.
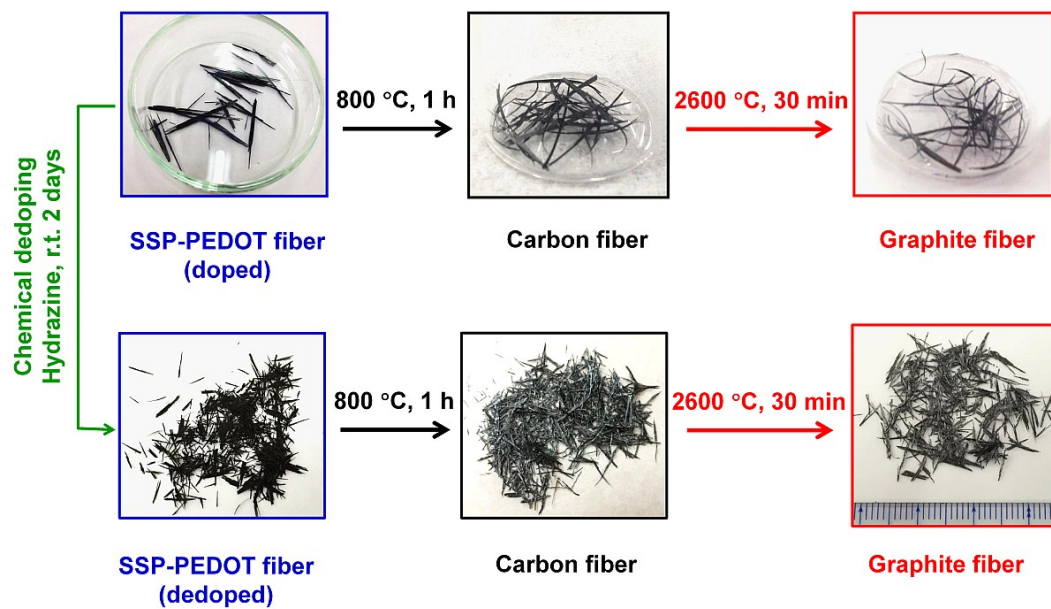
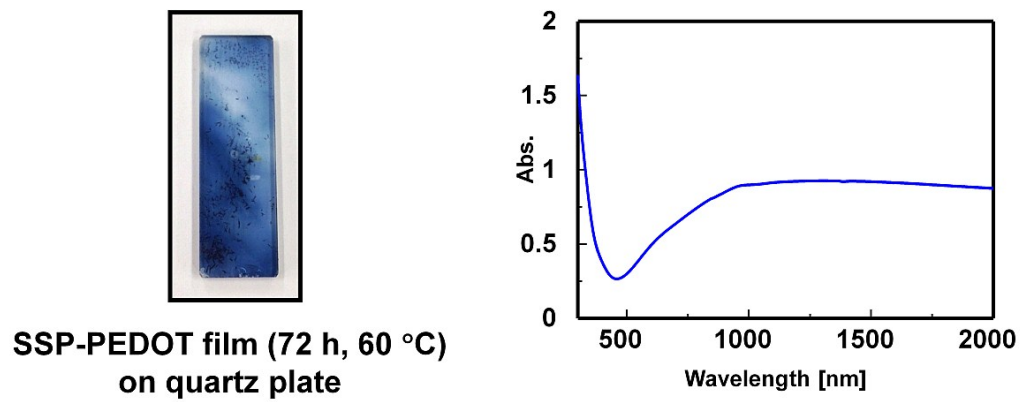**Fig. S4** Photographs of the SSP-PEDOT, carbon, and graphite fibers.

**SSP-PEDOT film (72 h, 60 °C)
on quartz plate**

Fig. S5 Photograph (left) and UV−vis−NIR spectrum (right) of the doped SSP-PEDOT film on quartz plate.
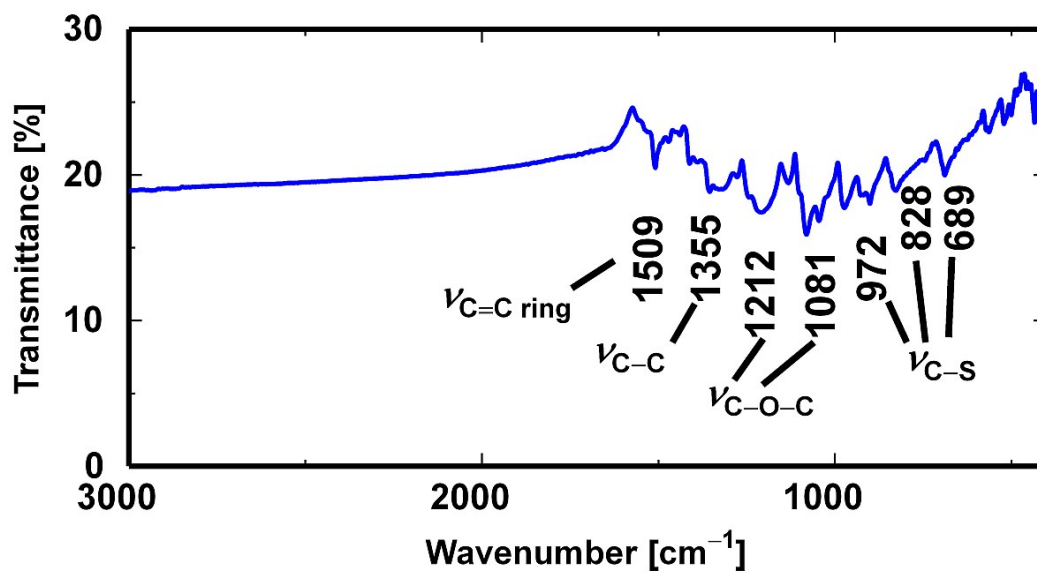
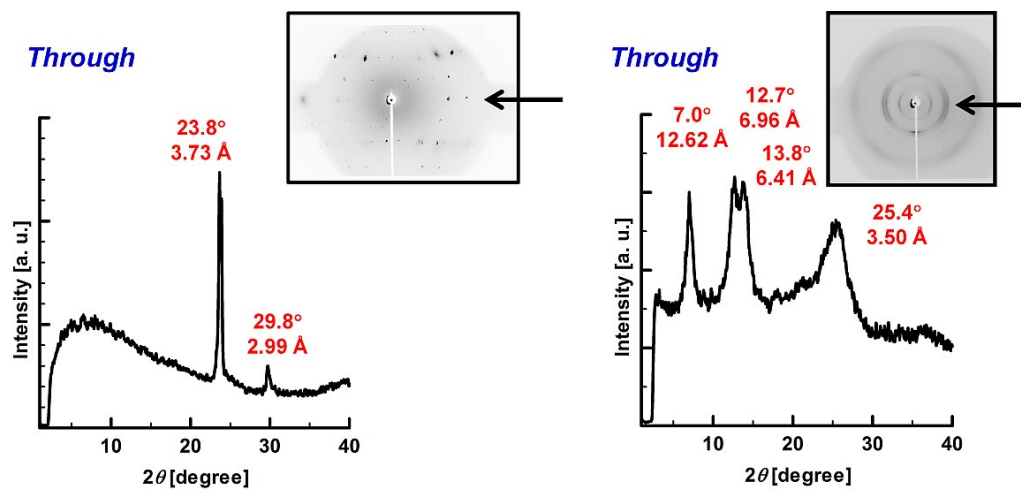**Fig. S6** IR absorption spectrum of doped SSP-PEDOT fibers.

Fig. S7 XRD patterns of the DBEDOT (left) and doped SSP-PEDOT (right) fibers in the through direction.
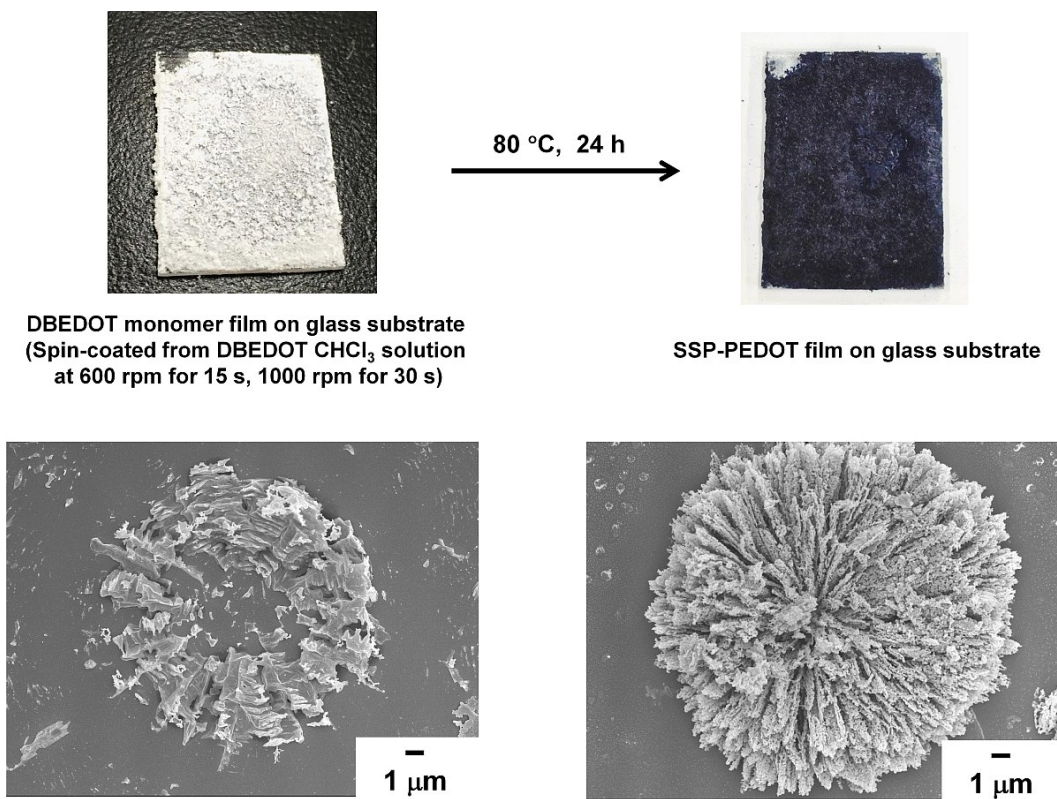
DBEDOT monomer film on glass substrate
(Spin-coated from DBEDOT CHCl₃ solution
at 600 rpm for 15 s, 1000 rpm for 30 s)

80 °C, 24 h

SSP-PEDOT film on glass substrate

1 μm

1 μm

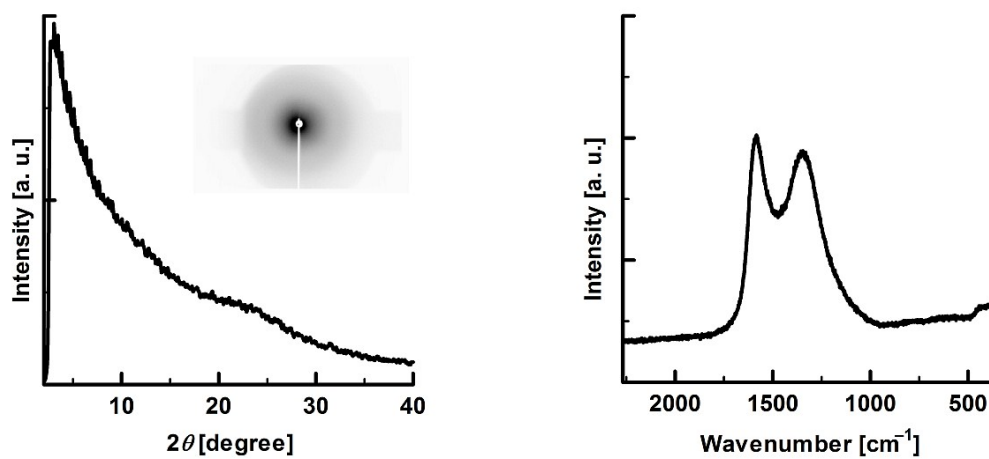**Fig. S8** Photographs (upper) and SEM images (lower) of the DBEDOT and doped SSP-PEDOT films.

Fig. S9 XRD patterns (left) and Raman scattering spectrum (right) of the carbon powder prepared at 800 °C for electrochemical tests.
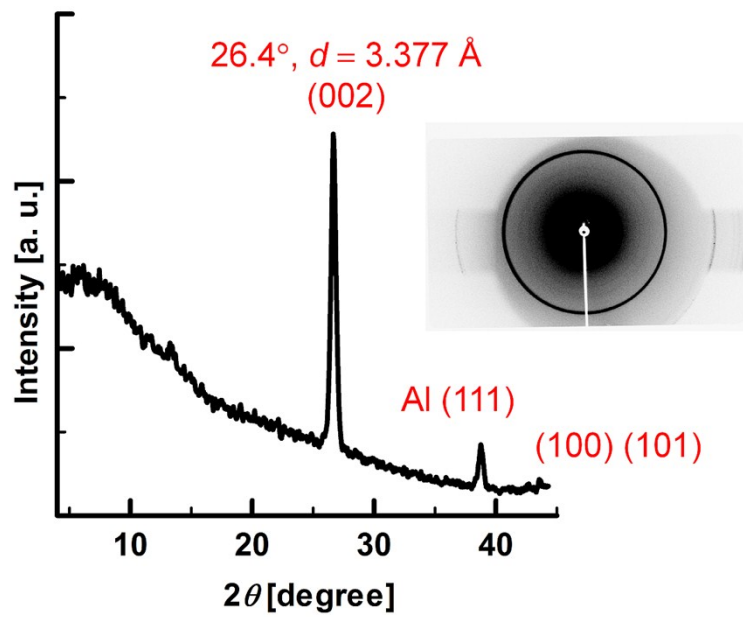
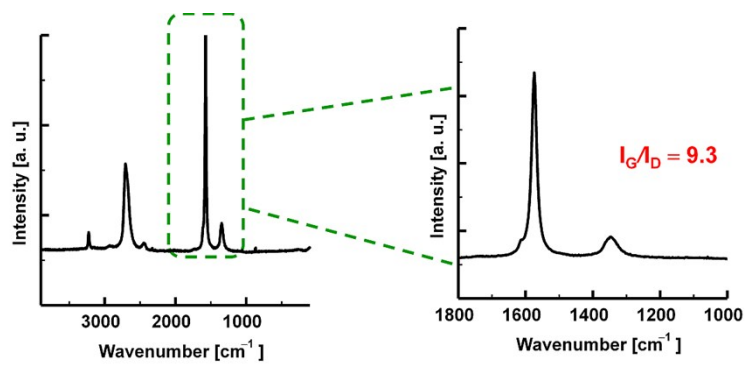**Fig. S10** XRD patterns of the Kish graphite powder.

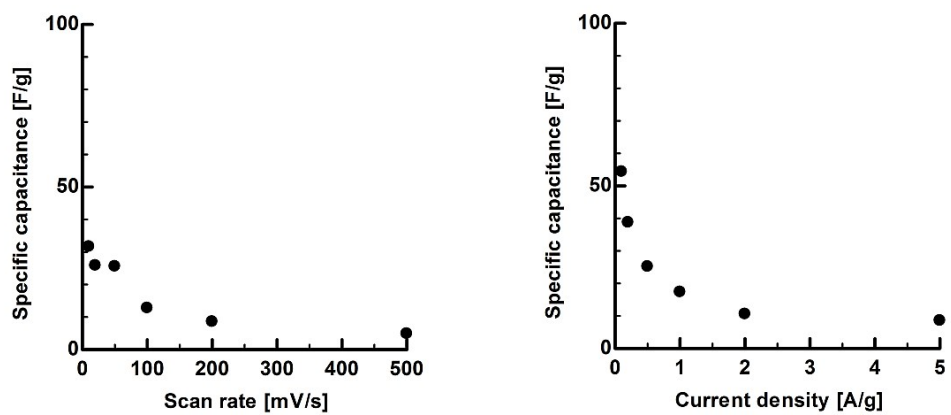**Fig. S11** Raman scatting spectra of the Kish graphite powder.

Fig. S12 Relationships between specific capacitance and (left) scan rate based on the CV curves and (right) current density based on GCD curves of the carbon films prepared from the doped SSP-PEDOT at 800 °C.

Table S1. Elemental analysis results of SSP-PEDOTs with various polymerization time.

Reaction time	Yield	C, %	H, %	S, %	Br, %	Calculated formula
1 day	80%	25.92	1.73	11.37	50.11	$[EDOT(Br^-)_{1.77}]_n$
7 days	74%	29.89	1.86	13.32	38.49	$[EDOT(Br^-)_{1.16}]_n$
7 days (Soxhlet)	56%	36.75	2.80	16.21	17.14	$[EDOT(Br^-)_{0.42}]_n$
dedoping	64%	36.84	3.35	17.32	5.62	$[EDOT(Br^-)_{0.13}]_n$

Table S2. Carbonization yields and elemental analysis results of carbon and graphite fibers prepared from doped and dedoped SSP-PEDOTs.

Precursor	Heat-treatment temperature (°C)	Yield	C, %	H, %	S, %	Br, %
Doped SSP-PEDOT	800	31%	78.82	0.25	18.75	0
	2600	79%	99.52	0	–	–
Dedoped SSP-PEDOT	800	38%	81.49	0.25	14.62	0
	2600	71%	100.00	0	–	–

Table S3. The structural parameters estimated from XRD patterns and Raman scattering spectra of graphite fibers as well as those of Kish graphite and graphite film.

Precursor	Form (direction)	d_{002} (Å)	$d_{100\ 101}$ (Å)	$I_{002}/I_{100\ 101}$	L_c (nm)	Number of graphite layers	I'_G/I'_D	L_a (nm)
Doped SSP-PEDOT	Fiber (edge)	3.3	2.1	341.1	31.6	95	5.4	17.9
	Fiber (through)	3.5	2.1	0.8	–	–		
	In powder	3.4	2.1	10.8	14.5	42		
Dedoped SSP-PEDOT	Fiber (edge)	3.3	2.1	241.6	16.6	50	3.7	10.9
	Fiber (through)	3.4	2.1	2.2	–	–		
	In powder	3.4	2.1	14.6	13.6	40		
Kish graphite	In powder	3.3	2.1	44.0	17.0	50	8.6	17.1
Doped PEDOT[5]	In film	3.5	2.1	23.5	5.5	16	1.9	8.1

Table S4. The summary of specific capacitances on the basis of the CV and GCD curves of the carbon film.

Scan rate (mV/s)	10	20	50	100	200	500
C_v (F/g)	31.7	25.9	25.6	12.8	8.6	4.9
Current density (A/g)	0.1	0.2	0.5	1.0	2.0	5.0
C_m (F/g)	54.4	38.8	25.2	17.4	10.6	8.6