Electronic Supplementary Information

Conjugated Polymer-based Carbonaceous Films as Binder-free Carbon Electrodes in Supercapacitors

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1. Materials and Measurements

1.1 Materials

The chemical compounds were purchased from commercially available sources and were used as received. Acetonitrile (ACN) (99.5%), hydrochloric acid (HCl), iodine (I_2), sodium (Na), sodium hydroxide (NaOH), potassium chloride (KCl), and 4 M potassium hydroxide (KOH) aq. were purchased from Nacalai Tesque, Inc. Calcium hydride (CaH_2) was purchased from Wako Pure Chemical Industries, Ltd. Tetra-*n*-butoxytitanium [Ti(O-*n*-Bu)$_4$] was purchased from Sigma-Aldrich Co., Ltd., and it was distilled under reduced pressure prior to use (b.p. = 206 °C/10 mmHg). Triethylaluminum (Et_3Al) was purchased from Nippon Aluminum Alkyls, Ltd. Tetra-*n*-butylammonium perchlorate (TBAP) and 3,4-ethylenedioxythiophene (EDOT) were purchased from Tokyo Chemical Industry Co., Ltd. Aluminum powder ($\phi = 0.1$ μm) and nickel plate [99+%, thickness (t) = 0.1 mm] were purchased from Nilaco Co., Ltd. ACN, ethanol (EtOH), and methanol (MeOH) (Nacalai Tesque, Inc.) were used as received. Toluene and tetrahydrofuran (THF) were distilled over sodium and calcium hydride as a drying agent under argon gas prior to use, respectively. EDOT was distilled under reduced pressure in argon gas atmosphere before use (b.p. = ~200 °C/760 mmHg, 112 °C/20 mmHg). KCl was recrystallized from aqueous solution before use. Acetylene gas of six-nine grade was purchased from Koatsu Gas Kogyo Co. Ltd. All experiments were performed under an argon (> 99.99% purity) atmosphere. Polyimide tape (P-221, t = 69 μm) was purchased from Nitto Denko, Co. Indium-tin oxide (ITO) glass was purchased from Furuuchi Chemical Co. (10 Ω/cm^2). Ag/AgCl reference electrode (saturated with KCl aq.), Hg/HgO reference electrode (1 M NaOH aq. as an electrolyte solution), and platinum (Pt) mesh electrode (80 mesh, $w \times l = 35 \times 25$ mm) were purchased from BAS, Inc. Pt counter electrode ($\phi \times l = 1 \times 10$ mm) was purchased from Metrohm Autolab. Pt counter electrode ($\phi \times l = 0.5 \times 50$ mm) was also purchased from BAS, Inc. Silver paste (D-550 or D-723S) was purchased from Fujikura Kasei Co., Ltd.

1.2 Measurements

Elemental analysis (EA) was performed at the Center for Organic Elemental Microanalysis of Kyoto University. Before the elemental analyses, poly(3,4-ethylenedioxythiophene) (PEDOT) films were dried via vacuum pumping for several hours at 80–90 °C (b.p. of ACN: 82 °C). The molecular ratio of doped perchlorate ion (ClO_4^-) to EDOT unit in the PEDOT film (ClO_4^-/EDOT) was calculated from the elemental analysis. The sum of all the elements is assumed to be 100%.

The thermal behaviors of PEDOT and polyacetylene (PA) films were investigated in heating runs performed up to 1000 °C at a heating rate of 10 °C/min in flowing nitrogen (> 99.99%, 100 ml/min) or oxygen (> 99.8%, 20 ml/min) gas using a thermogravimetric–differential thermal analysis (TG–DTA) apparatus (TG-DTA6200, Seiko or STA 8000, Perkin Elmer) with Pt or alumina pans.

X-ray diffraction (XRD) measurements were performed using a Rigaku ultra-X18 diffractometer. XRD patterns were recorded using an X-ray generator with Ni-filtered Cu Kα radiation (30 kV/300 mA: $\lambda = 1.54$ Å) and a flat-plate camera (RINT2500, Rigaku). The sample-to-film distance was 100 mm as calibrated using the (111) face of aluminum ($d = 2.33787$ Å), and the exposure time was 60–123 min. Diffraction patterns were recorded using an imaging plate and scanned by a RAXIA-Di imaging plate reader at 100 μm resolution.

Raman spectra were obtained at room temperature using a spectroscope with a single monochromator and a charge-coupled device (CCD) detector cooled by a Peltier device (NRS-4100, JASCO), which was calibrated using a polystyrene standard. A 0.7 mW laser with a wavelength of 532 nm was used. The exposure time was 180 sec (90 sec × 2). The crystal sizes along the *a*-axis (L_a) of the carbonaceous films were estimated from the Raman spectra using the following equation: $L_a = 4.35(I'_D/I'_G)^{-1}$, where I'_D and I'_G are the integrated intensities of the D- and G-bands, respectively.[1,2] Raman spectra were fitted by using a mixed Gaussian-Lorentzian function with the software PeakFit®.

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

The electrical conductivities of the PEDOT, PA, and carbonaceous films were measured at room temperature using a low resistivity meter, Loresta GP with a MCP-TP06P probe (Mitsubishi Chemical Analytech).

Infrared (IR) absorption spectra of the PEDOT and PA films were recorded in film or powder form with a JASCO FT (Fourier transform)-IR 4200 spectrometer using transmission or attenuated total reflection (ATR) mode. When the sample is measured in powder form, the measurement was performed using the KBr method. The *cis* content of the PA film was evaluated using the following equation: *cis* content (%) = 100[1.30A_{cis}/(1.30A_{cis} + A_{trans})], where A_{cis} and A_{trans} represent the absorbances of the 740 and 1015 cm^{-1} bands in the spectrum of a specimen, respectively.[3]

Nitrogen adsorption/desorption isotherms of the carbonized PEDOT and PA films were obtained at 77 K using a 3Flex (Micromeritics Instrument Corp.). The samples were degassed under vacuum at 200 °C for 2 h before the measurement. The specific surface area was determined using the Brunauer−Emmett−Teller (BET) method in the relative pressure (P/P_0) range of 0.006−0.035 for the carbonized PEDOT film at 1000 °C, 0.006−0.025 for the carbonized PEDOT film at 1100 °C, and 0.005−0.012 for the carbonized PA film in the range of 1000−1100 °C. The pore size distributions of the samples were calculated using the density functional theory (DFT) method (slit pore model). The micropore surface area (S_{micro}) and micropore volume (V_{micro}) were evaluated using the *t*-plot method. The total pore volume (V_{total}) was obtained at $P/P_0 = 0.99$. The average pore diameter (D_{average}) was calculated using the following equation: $D_{\mathrm{average}} = 4V_{\mathrm{total}}/S_{\mathrm{BET}}$.

For transmission electron microscopy (TEM), the carbonized PEDOT was dispersed in EtOH with ultrasonic treatment, and the dispersion was dropped on a Cu mesh (Oken Shoji). Selected-area electron-diffraction (SAED) patterns were used to identify the crystalline phases of the samples. The accelerating voltage of the TEM (JEM-2100F, JEOL) was 200 kV.

The accelerating voltage of the field emission (FE)-SEM (JSM-7500F, JEOL) was 5 kV. The PEDOT and PA films were coated with the Pt of a Pt-Pd alloy using a JFC-1600 (JEOL) ion coater prior to SEM measurements. The coating thickness was determined to be ca. 5 nm.

Carbonization was performed using an electric furnace (KDF75, Denken or ARF-50KC, ASH). The PEDOT and PA films were placed between carbon plates (*w* × *l* × *t* = 80 × 80 × 2 mm) which were then transferred into the electric furnace. The polymer film was then carbonized at 600–1100 °C using the electric furnace for 30–60 min in flowing argon (> 99.999%, 1 l/min) or nitrogen (> 99.9999%, 200 ml/min) gas. A heat treatment time of 180 min was adopted only for the samples for the cyclability tests. The heating rate was 5–10 °C/min. The carbonization yield was determined using the equation: 100[(weight of carbonized PEDOT or PA film)/(weight of PEDOT or PA film)].

The electrochemical polymerization was performed using 0–30 V 2.5 A direct current (DC) power supply (CPS-3025L, CUSTOM).

Electrochemical measurements were performed in a three-electrode system at room temperature using an μ-AUTOLAB III or PGSTAT302N potentiostat (Metrohm Autolab), running NOVA software (ver.1 or ver.2). Pt wire and a Ag/AgCl electrode or Hg/HgO electrode were used as counter and reference electrodes, respectively. A nickel plate (*w* × *l* × *t* = 8–13 × 25 × 0.1 mm) was used as a current collector. The PEDOT-based carbonaceous film (*w* × *l* = 6–10 × 8–10 mm) was weighed, and then the glass side of the film was attached to the nickel plate with a silver paste. The sample for the PA-based carbon film (*w* × *l* = 12–13 × 12–13 mm) was prepared similar to that for the PEDOT-based carbonaceous film. After drying at room temperature for over 2 h or at 100 °C for 30 min, the sample was immersed in 5 M KCl aq. or 4 M KOH aq. All electrolyte solutions were prepared with purified water (Direct-Q 3 UV, σ = 0.056 μS/cm at 25 °C or PURELAB Option-R 7, 15 MΩ cm at 25 °C). The air bubbles trapped in the porous sites of the carbon electrode were removed via vacuum pumping, and after degassing, the sample was kept in solution overnight so that the porous space became filled with the electrolyte solution. The electrolyte solution was exposed nitrogen bubbling (> 99.99%) for 5–10 min to remove oxygen gas from the solution. The specific capacitance ($C_{m,\mathrm{CV}}$) was calculated from the cyclic voltammograms using the following equation: $C_{m,\mathrm{CV}} = C/m = \int I(V)dV/2\Delta Vmv$, where $C_{m,\mathrm{CV}}$ is the specific gravimetric capacitance of the carbonaceous film, m is the mass loading on the current collector, $\int I(V)dV$ is the area in the CV curve, ΔV is the potential window in the CV curve, v is the scan rate. The specific capacitance ($C_{m,\mathrm{GCD}}$) values were calculated from the discharge curve of the galvanostatic charge and discharge (GCD) curves using the following equation: $C_{m,\mathrm{GCD}} = C/m = I\Delta t/\Delta Vm$, where $C_{m,\mathrm{GCD}}$ is the specific gravimetric capacitance of the carbonaceous film, m is the mass loading on the current collector, Δt is the discharge time, ΔV is the potential change in the GCD curve (excluding the IR drop). The energy density and power density of the carbonaceous film electrodes prepared in the range of 1000–1100 °C were calculated using the following equations: $E = C_{\mathrm{m,GCD}} \times \Delta V^2 \times 1000/2 \times 3600$, $P = E \times 3600/\Delta t$, where E and P are the energy density and power density of the three-electrode cell, respectively. Electrochemical impedance spectra were recorded in the frequency range of 0.1–100000 Hz with a 10 mV RMS perturbation voltage.

2. Polymerization of Mono-EDOT in ACN

The electrochemical polymerization of mono-EDOT was performed in ACN in a glass container ($w \times$

$l \times h = 30 \times 65 \times 75$ mm). The polymerization of the monomer was performed using ITO glass as a working electrode (anode) and Pt mesh as a counter electrode (cathode) at room temperature while stirring at 300 rpm. ITO glass was cut into 50 × 50 mm squares and were ultrasonicated in EtOH for over 20 min, followed by drying at room temperature before the polymerization reaction. The distance between the anode and the cathode was ca. 10 mm. The concentrations of the monomer and supporting electrolyte (TBAP) were 0.05 M. The amount of the ACN solution was 70 ml. The polymerization voltage and the polymerization time were 4 V and 60 min, respectively. A polymerization time of 90 min was adopted for the samples for BET and TEM measurements. The PEDOT film was washed with hexane, MeOH, and ACN in this order at ambient temperature. The film was dried on a Teflon (polytetrafluoroethylene) sheet ($t = 0.2$ mm) at 80–90 °C for several hours by vacuum-pumping. The thickness of the film was 163 ± 31 μm. Elemental analysis indicated that the PEDOT film had carbon, hydrogen, sulfur, and chlorine contents of 40.38, 2.75, 18.06, and 5.53 wt. %, respectively (Calcd. C 51.42, H 2.88, O 22.83, S 22.87.). The bulk density (d_{bulk}) of the PEDOT film was 0.52 g/cm^3. The electrical conductivity of the PEDOT film was 16 ± 6 S/cm ($t = 163 \pm 31$ μm) at room temperature.

3. Synthesis of PA Film

All experiments were performed under an atmosphere of argon gas of six-nine grade. PA films were synthesized as follows. Toluene was used as a solvent for the Ziegler–Natta catalyst: tetra-*n*-

butoxytitanium, Ti(O-*n*-Bu)$_4$, and triethylaluminum, Et$_3$Al. The total amount of solvent was 2 ml. The typical concentration of [Ti] was ~0.4 mol/l, and the mole ratio of the cocatalyst-to catalyst [Al]/[Ti] was approximately 4. The catalyst solution was aged for 110 min in a Schlenk flask at ambient temperature. The catalyst solution was coated onto the inner wall of the Schlenk flask by slowly rotating the flask after aging. The flask was connected to a vacuum line via a flexible joint and then degassed. Interfacial polymerization was performed by introducing acetylene gas into the catalyst solution. Acetylene gas of six-nine grade was used without further purification. The polymerization temperature was maintained at −78 °C by immersing the Schlenk flask into a dry ice–ethanol bath. The initial acetylene pressure was 424 Torr. The polymerization was stopped when the pressure decreased by 84 Torr. The polymerization time was 60 min. The resulting PA film was carefully stripped from the container and washed with purified toluene, a MeOH solution containing 1 N HCl, and THF sequentially. The film was dried by vacuum-pumping for >2 h and was stored in a freezer at −20 °C. The thickness of the film was 99 ± 1 μm. Elemental analysis indicated that the PA film had carbon and hydrogen contents of 88.27 and 7.48 wt. %, respectively (Calcd. C 92.26, H 7.74.). The d_{bulk} value of the PA film was 0.72 g/cm^3. The porosity (P) of the PA film was estimated to be 38% using the following equation: $P\ (\%) = 100[1 - (d_{\mathrm{bulk}}/d_{\mathrm{true}})]$, where d_{bulk} is the bulk density of the film and d_{true} is the true density of PA (1.16 g/cm^3).[4] The present PA film had a *cis* content of 80% (Fig. S4). The electrical conductivity of the PA film was 338 ± 7 S/cm (t = 99 ± 1 μm) after iodine doping ($[\mathrm{CHI}_{0.31}]_n$) at room temperature.

4. IR Absorption Spectra of PEDOT and PA Films

The IR absorption spectrum of the PEDOT film was recorded using the KBr method (Fig. S4a) and showed broad bands characteristic of p-type doped PEDOTs at approximately 1000–1500 cm^{-1}.[5] In contrast, the PA film was examined by using ATR-IR absorption spectroscopy (Fig. S4b). The *cis* content of the PA film was determined from the absorption bands at 740 and 1015 cm^{-1} attributed to *cis* and *trans* C–H out-of-plane vibrations, respectively. The present PA film had a *cis* content of 80% due to the low polymerization temperature of −78 °C.[3]

Supplementary References

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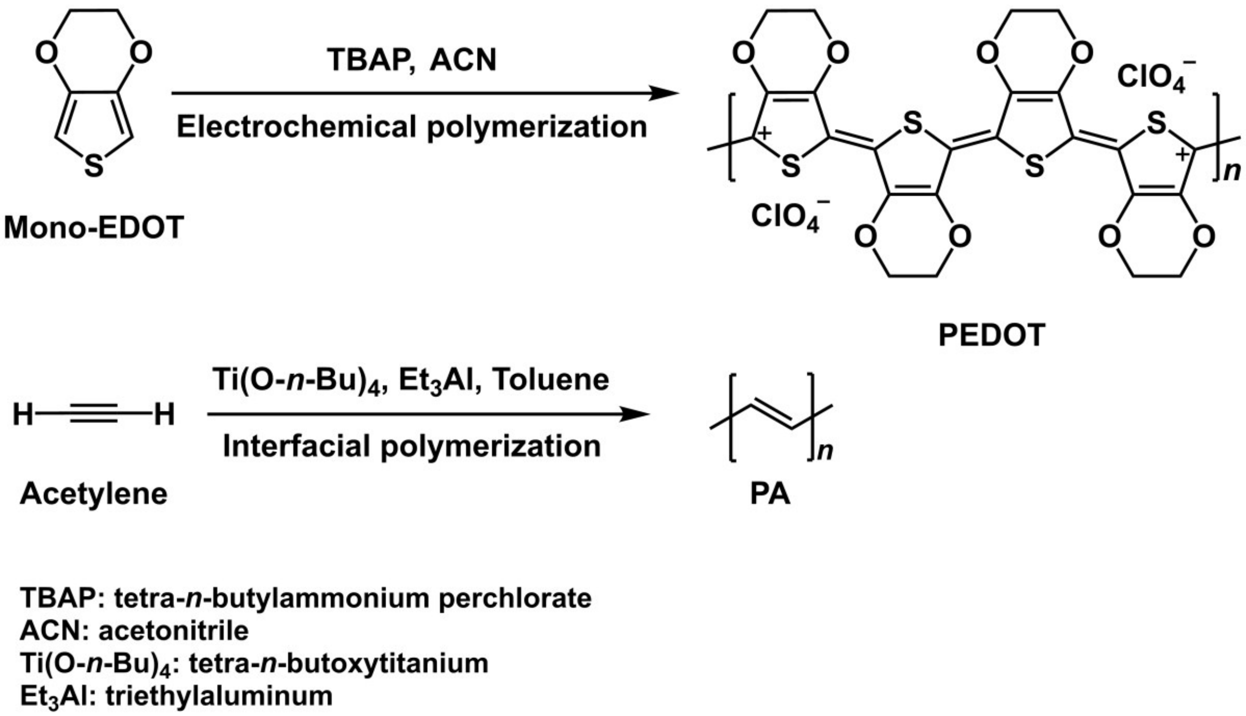
Supplementary Figures



Scheme S1 Synthetic routes of PEDOT and PA.

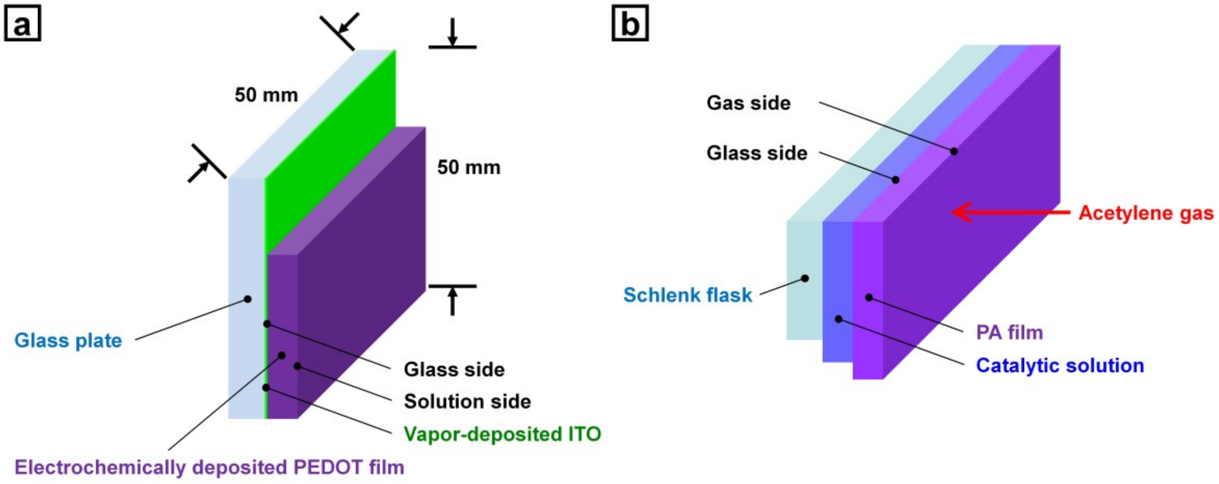


Fig. S1 (a) Solution and glass sides of an electrochemically synthesized PEDOT film. (b) Gas and glass sides of a PA film.

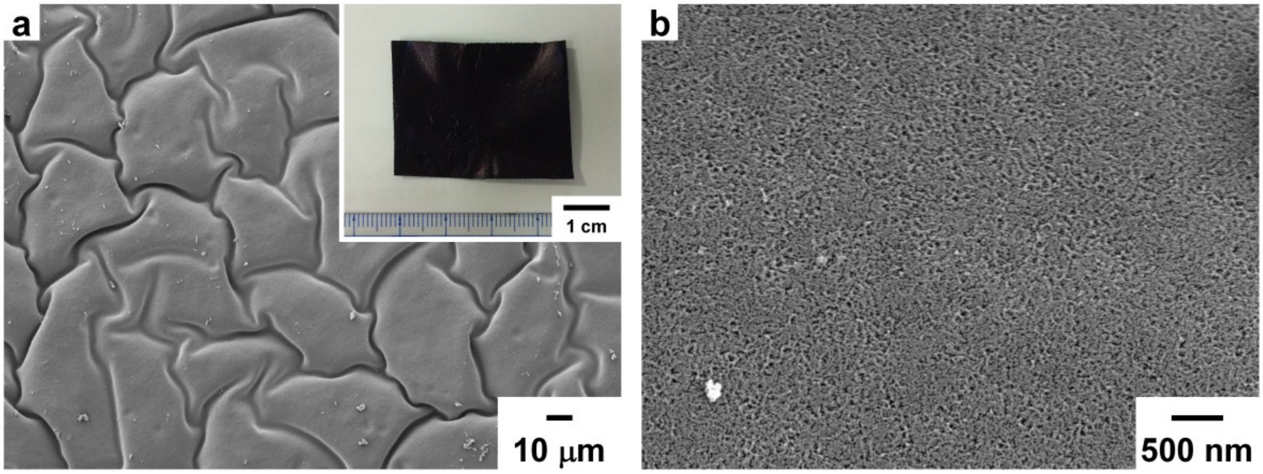


Fig. S2 (a,b) SEM images of the glass side of the PEDOT film. The inset shows a photograph of the glass side of the PEDOT film.

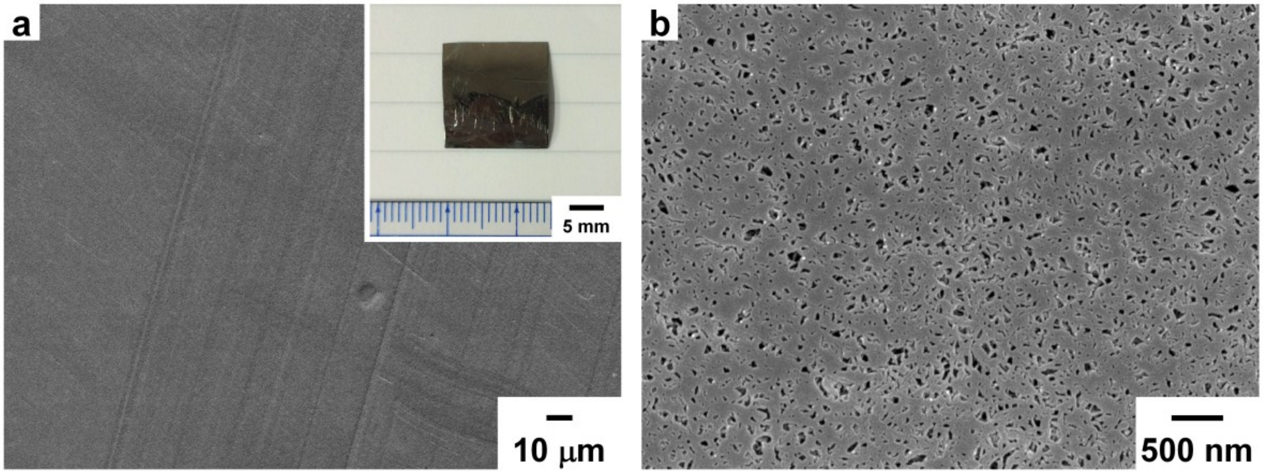


Fig. S3 (a,b) SEM images of the glass side of the PA film. The inset shows a photograph of the glass side of the PA film.

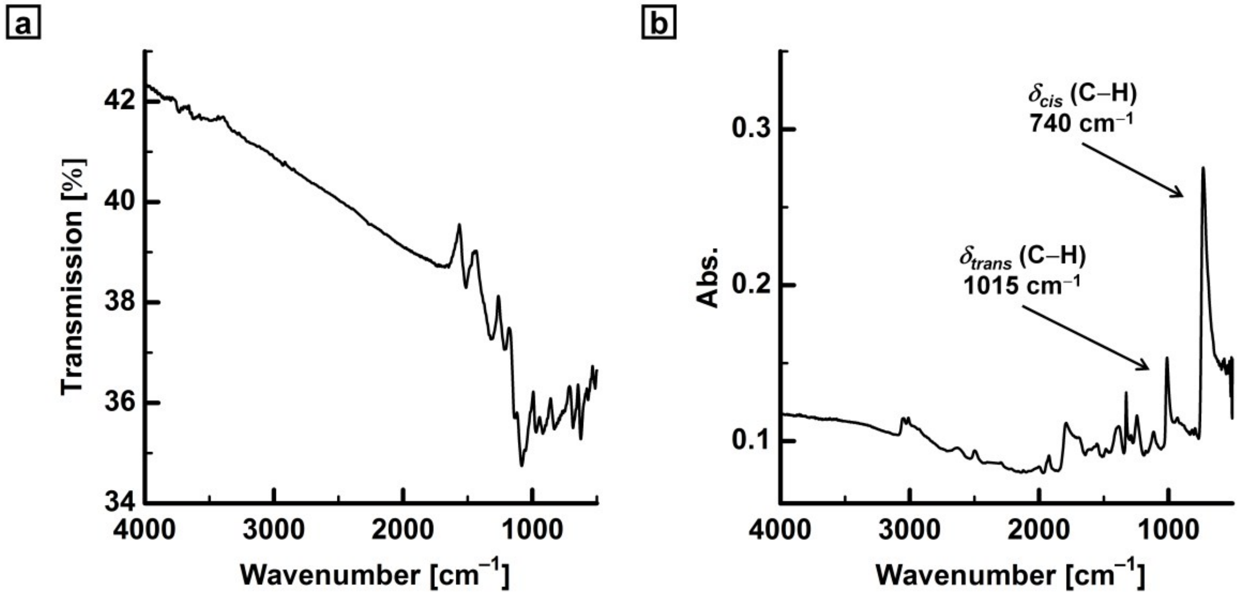


Fig. S4 (a) IR absorption spectrum of the PEDOT film. (b) ATR-IR absorption spectrum of the PA film. The *cis* content of 80% was calculated from the absorption bands at 740 and 1015 cm^{-1} attributed to *cis* and *trans* C–H out-of-plane vibrations, respectively.

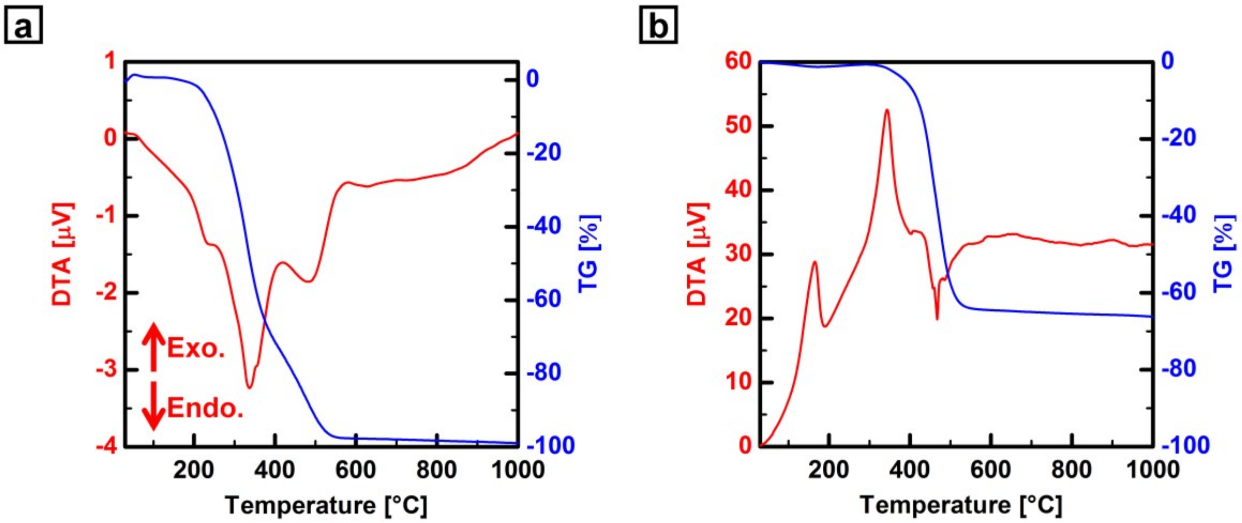


Fig. S5 (a) TG–DTA curve of the ClO_4^--doped PEDOT film obtained under oxygen gas. The film was stable up to the temperature of 215 °C and decomposition of the film occurs in the region between 215 °C and 528 °C.[6] The initial weight decrease (<77.9 °C) in the TG curve was attributed to an adsorbed moisture evaporation from the film. (b) TG–DTA curve of the pristine PA film ($[CH]_n$) obtained under nitrogen gas. The DTA curve presents exothermic peaks at 165 °C and 343 °C and an endothermic peak in the range of 400–600 °C. These peaks are attributed to a *cis*–*trans* isomerization, cross-linking, and thermal decomposition, respectively.[7] The decomposition was accompanied by a large weight loss (65% at 600 °C) of the PA film due to the volatilization of hydrocarbon gases, as shown in the TG curve.

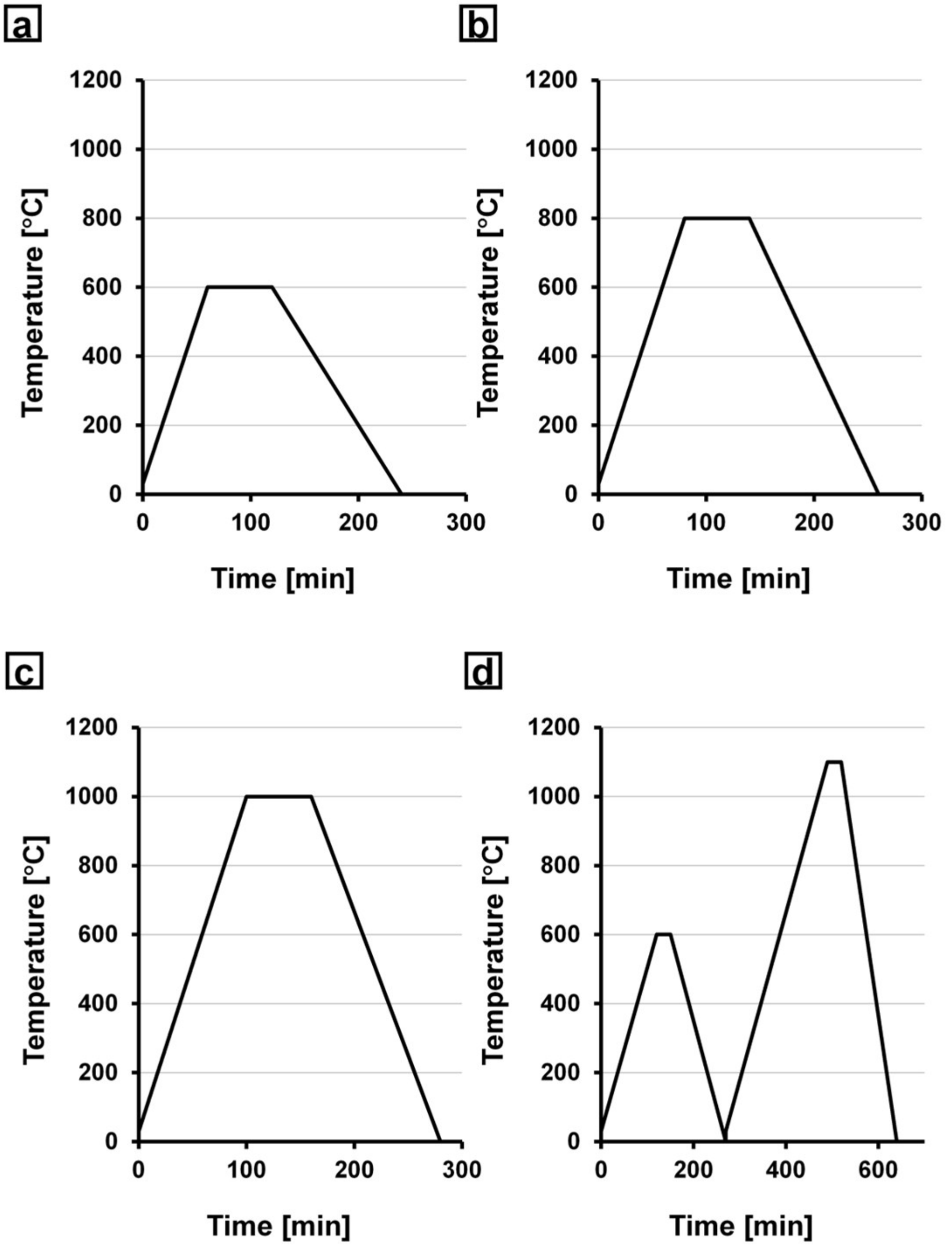


Fig. S6 Heat-treatment programs during carbonization at (a) 600, (b) 800, (c) 1000, and (d) 1100 °C.

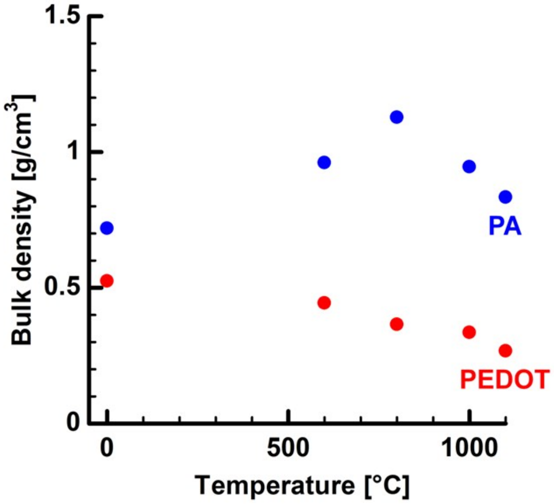


Fig. S7 d_{bulk} values of the PEDOT, PA, and carbonaceous films as a function of heat-treatment temperature.

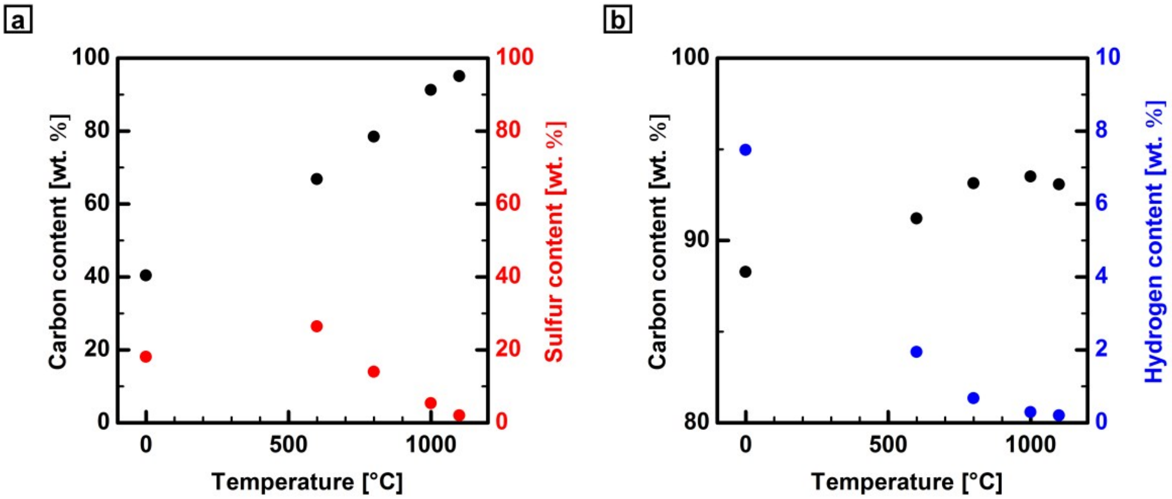


Fig. S8 (a) Carbon and sulfur contents of the PEDOT and carbonaceous films as a function of heat-treatment temperature. (b) Carbon and hydrogen contents of the PA and carbon films as a function of heat-treatment temperature.

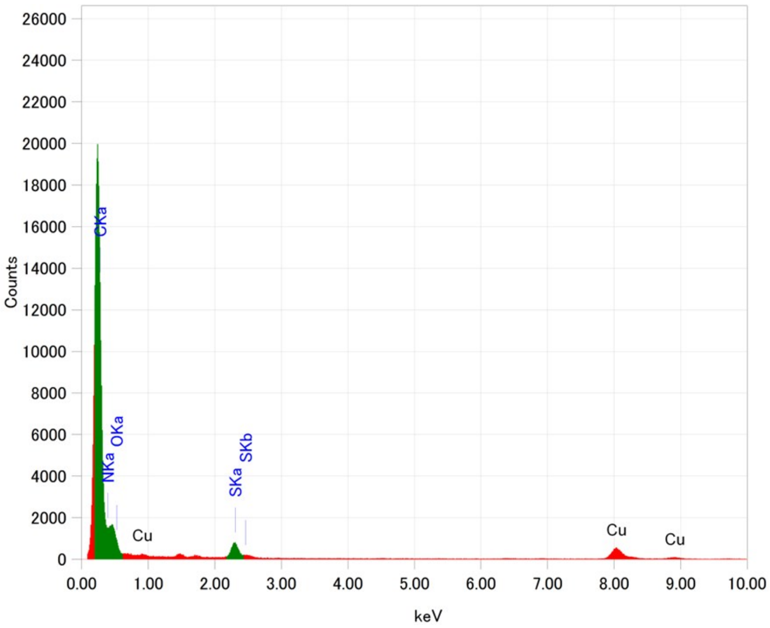


Fig. S9 TEM-EDS (energy dispersive X-ray spectrometry) analysis of the PEDOT film carbonized at 1100 °C. Peaks labelled Cu originate from the TEM grid.

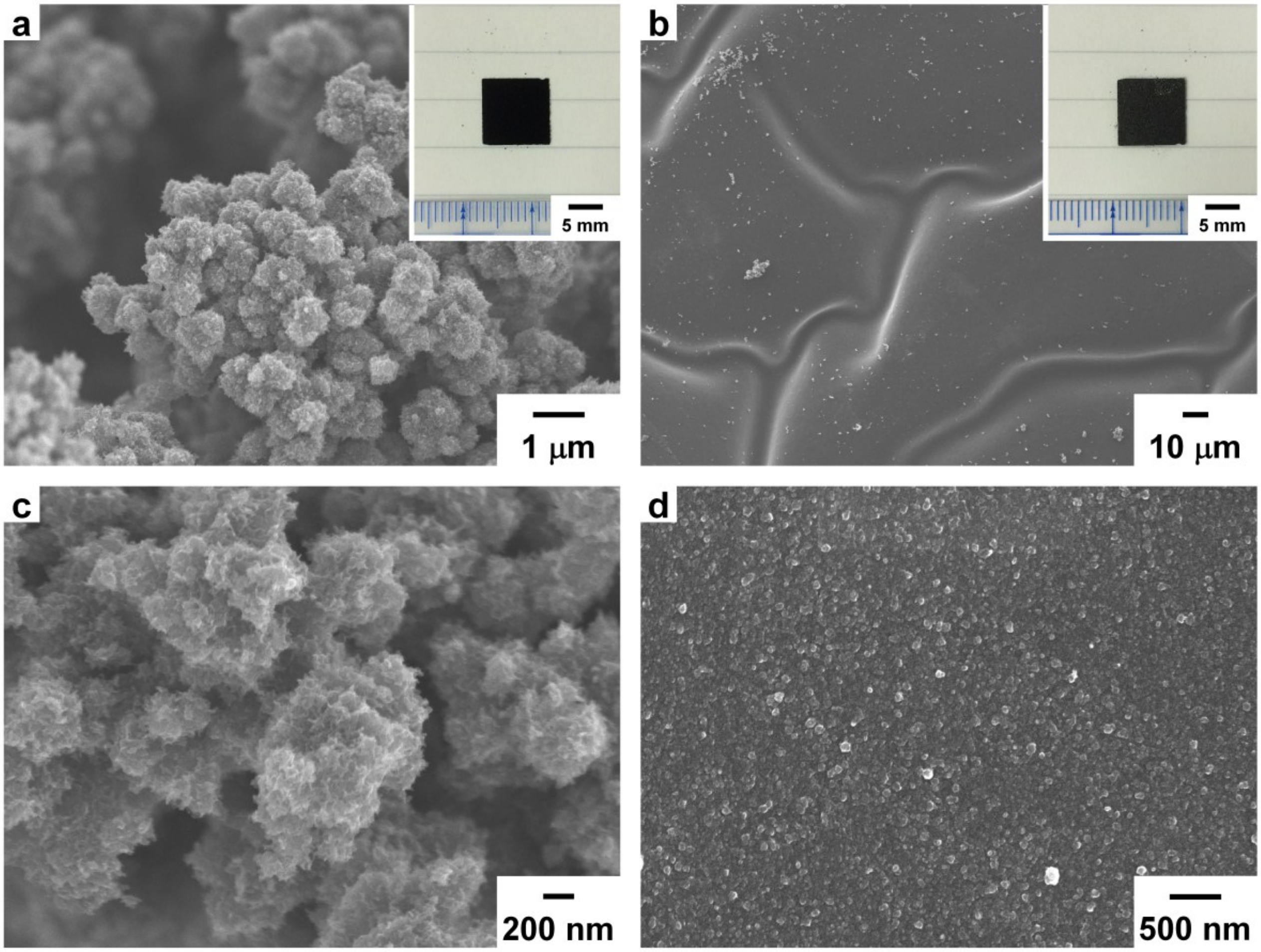


Fig. S10 SEM images of the (a,c) solution and (b,d) glass sides of the PEDOT film carbonized at 600 °C. The insets show photographs of the PEDOT film carbonized at 600 °C [$w \times l = 10 \times 10$ mm, $t = 144 \pm 5$ μm, $d_{\mathrm{bulk}} = 0.44$ g/cm^3, electrical conductivity (σ) = $6.1 \times 10^{-6} \pm 9.9 \times 10^{-7}$ S/cm]. (a) Solution side and (b) glass side.

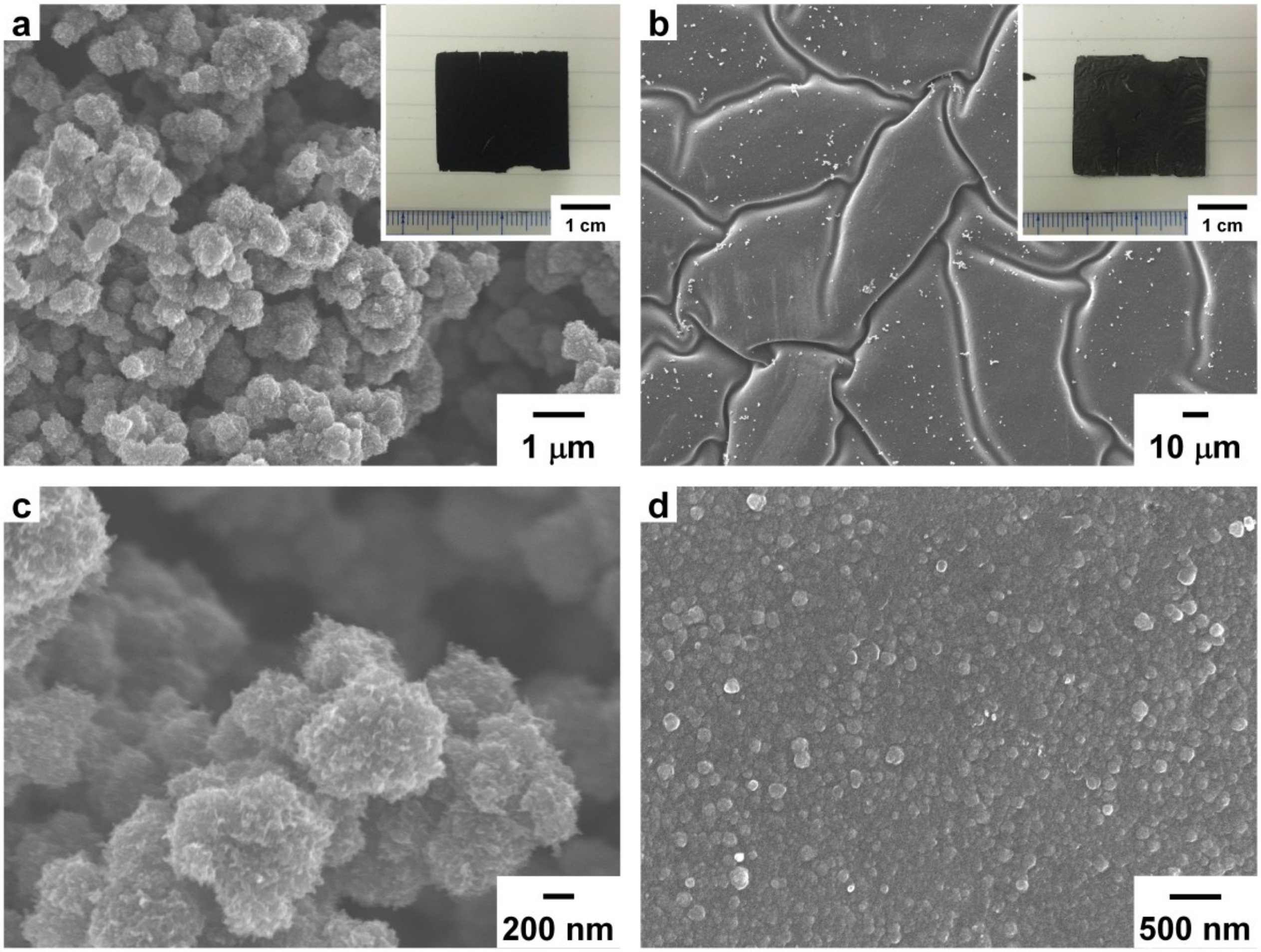


Fig. S11 SEM images of the (a,c) solution and (b,d) glass sides of the PEDOT film carbonized at 800 °C. The insets show photographs of the PEDOT film carbonized at 800 °C ($t = 121 \pm 36$ μm, $d_{\mathrm{bulk}} = 0.36$ g/cm^3, $\sigma = 1.4 \times 10^{-1} \pm 3.2 \times 10^{-2}$ S/cm). (a) Solution side and (b) glass side.

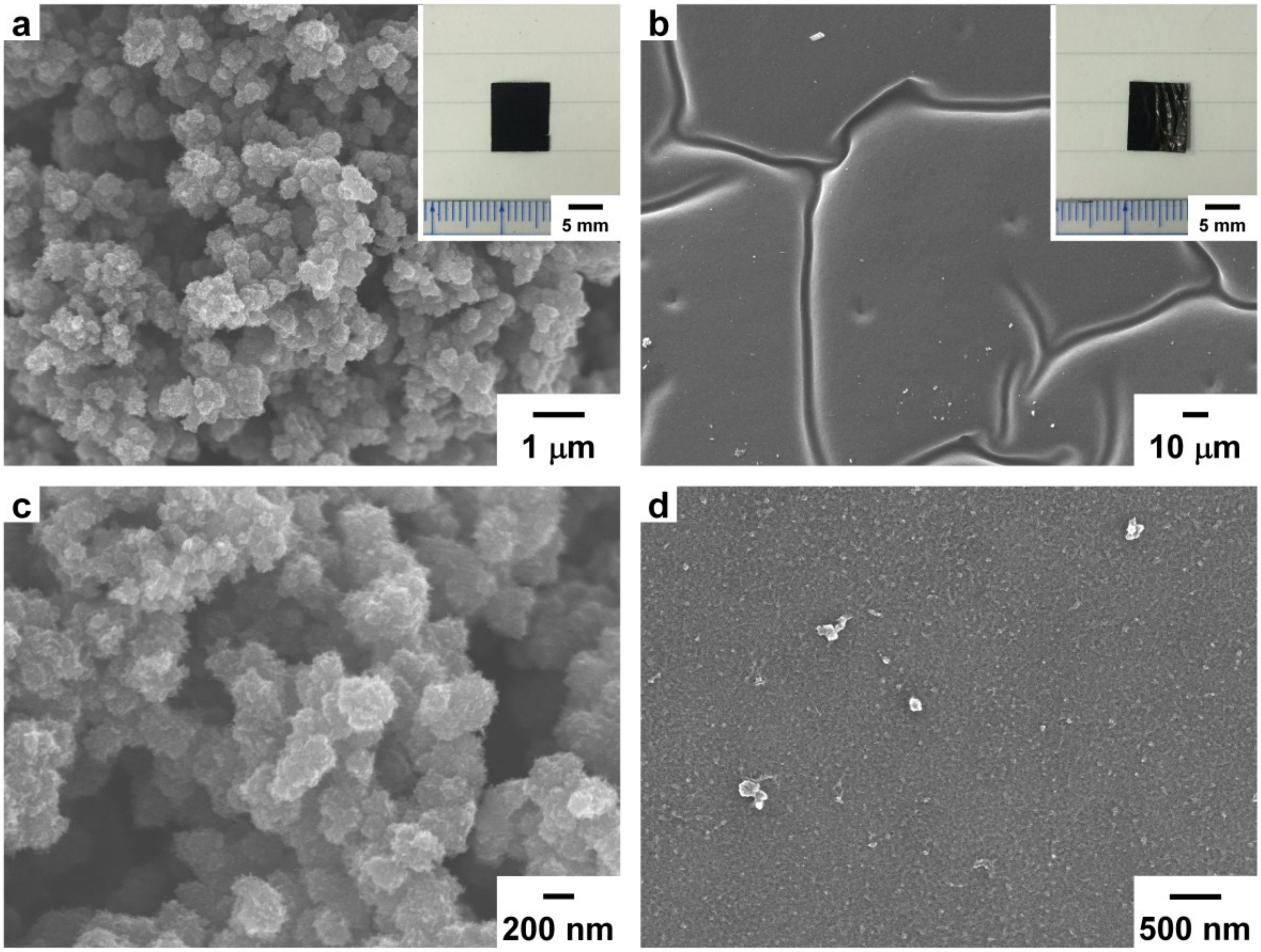


Fig. S12 SEM images of the (a,c) solution and (b,d) glass sides of the PEDOT film carbonized at 1000 °C. The insets show photographs of the PEDOT film carbonized at 1000 °C ($w \times l = 8.0 \times 10$ mm, $t = 64 \pm 7$ μm, $d_{\mathrm{bulk}} = 0.34$ g/cm^3, $\sigma = 1.6 \pm 0.1$ S/cm). (a) Solution side and (b) glass side.

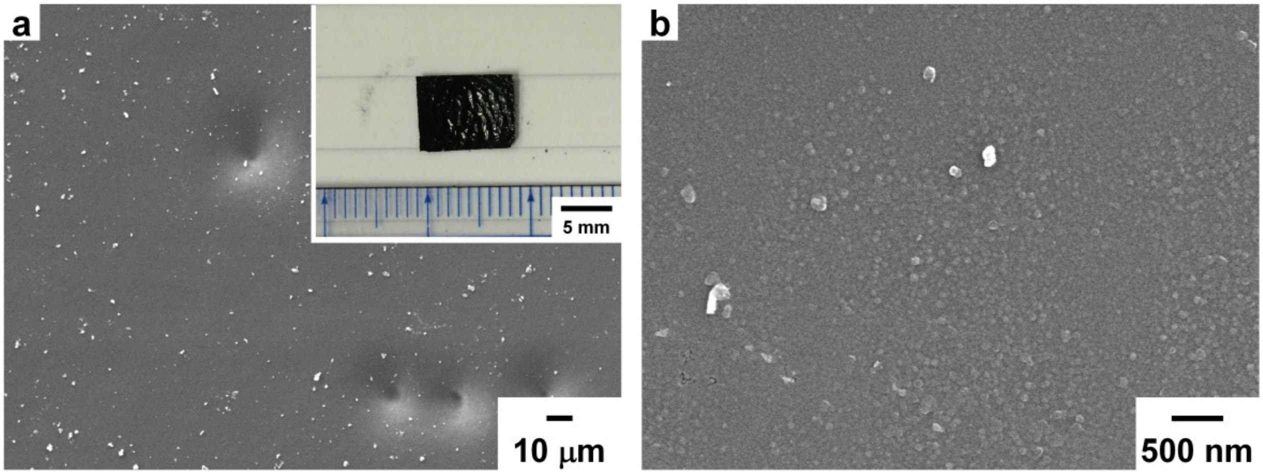


Fig. S13 (a,b) SEM images of the glass side of the PEDOT film carbonized at 1100 °C. The inset shows a photograph of the glass side of the carbonaceous film.

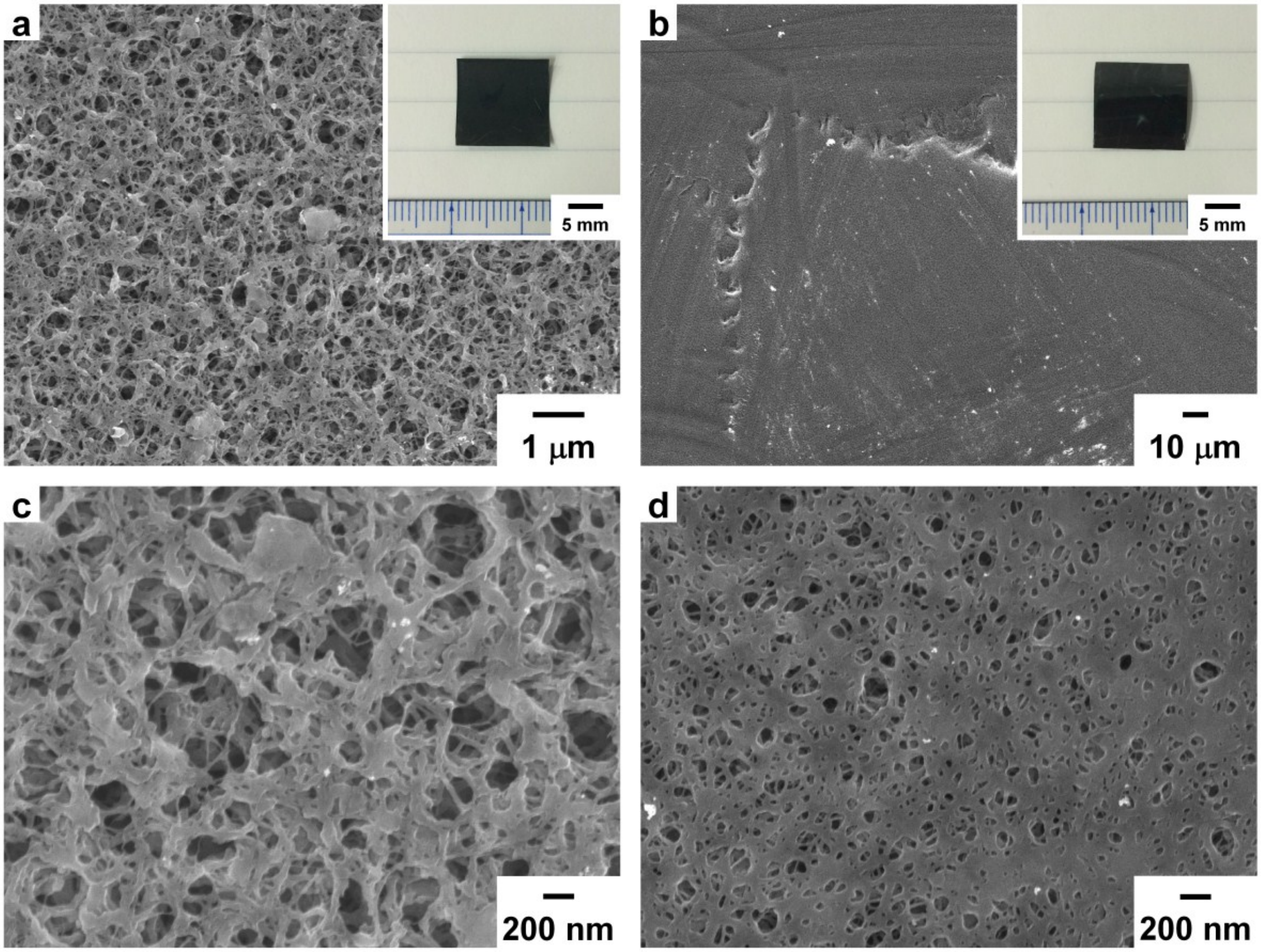


Fig. S14 SEM images of the (a,c) gas and (b,d) glass sides of the PA film carbonized at 600 °C. The insets show photographs of the carbon film ($w \times l = 13 \times 13$ mm, $t = 76 \pm 1$ μm, $d_{\mathrm{bulk}} = 0.96$ g/cm^3, $\sigma = 2.1 \times 10^{-3} \pm 4.6 \times 10^{-5}$ S/cm). (a) Gas side and (b) glass side.

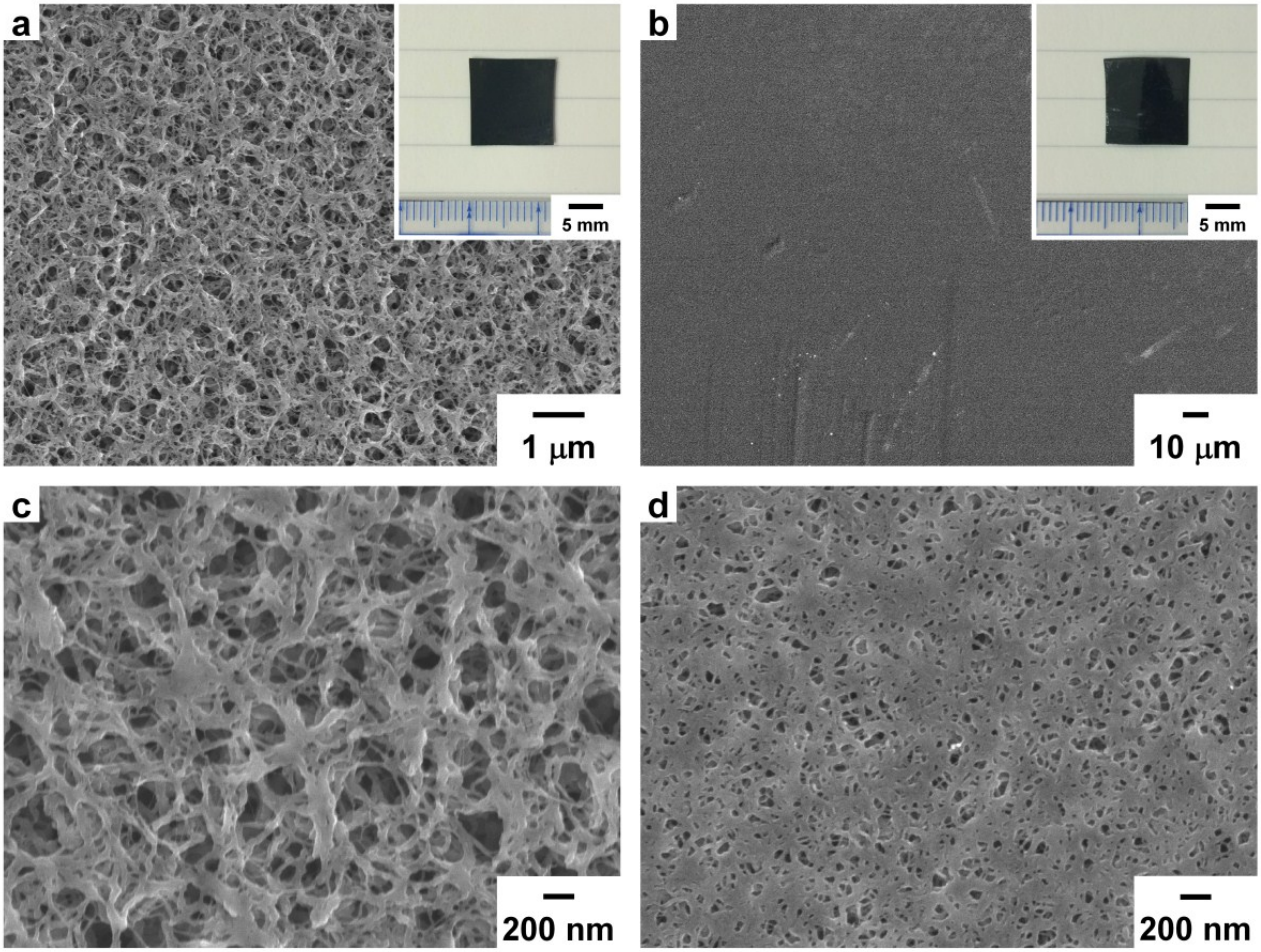


Fig. S15 SEM images of the (a,c) gas and (b,d) glass sides of the PA film carbonized at 800 °C. The insets show photographs of the carbon film ($w \times l = 12 \times 13$ mm, $t = 66 \pm 1$ μm, $d_{\text{bulk}} = 1.13$ g/cm^3, $\sigma = 38 \pm 1$ S/cm). (a) Gas side and (b) glass side.

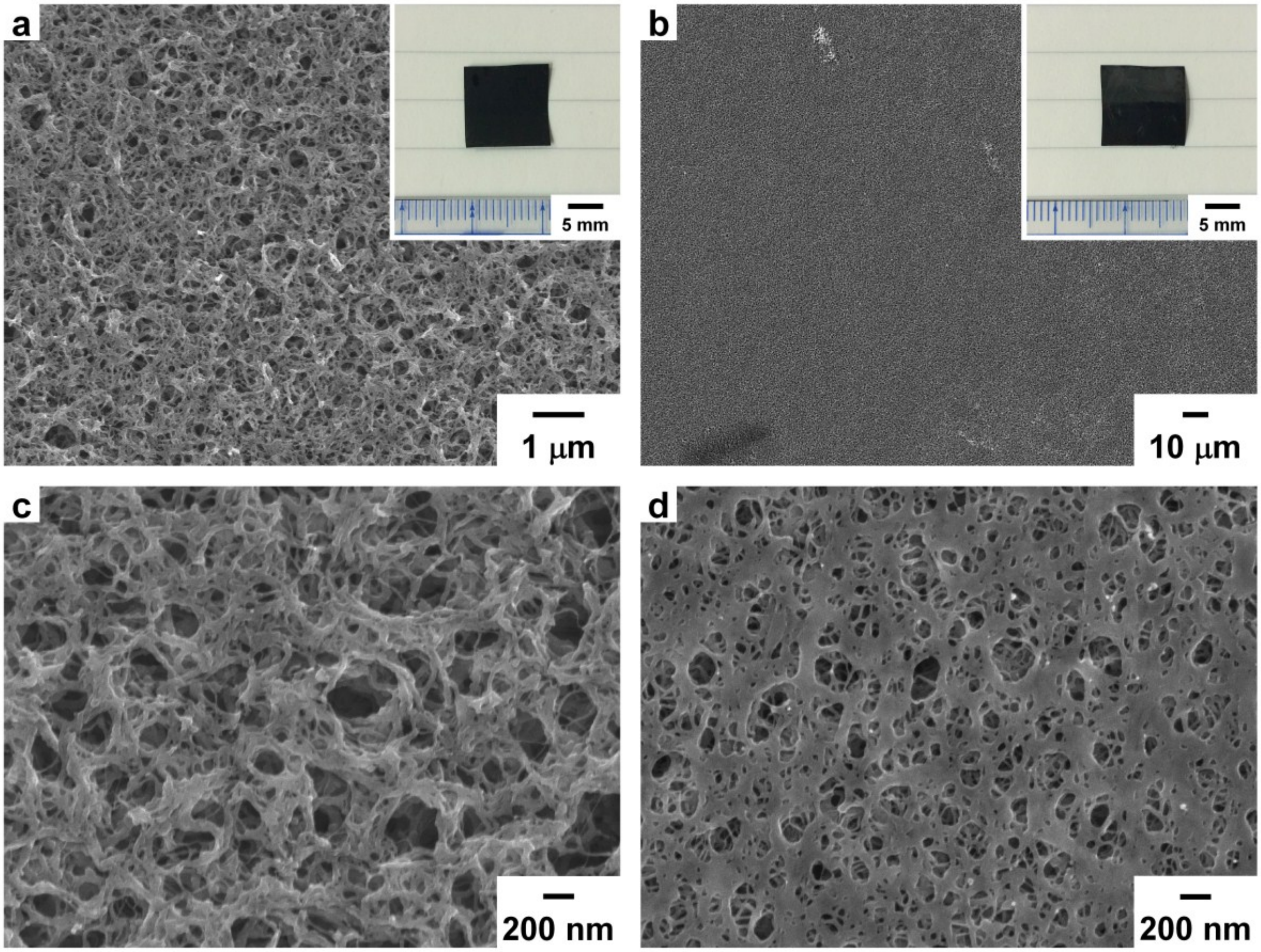


Fig. S16 SEM images of the (a,c) gas and (b,d) glass sides of the PA film carbonized at 1000 °C. The insets show photographs of the carbon film ($w \times l = 12 \times 12$ mm, $t = 66 \pm 3$ μm, $d_{\text{bulk}} = 0.95$ g/cm^3, $\sigma = 97 \pm 5$ S/cm). (a) Gas side and (b) glass side.

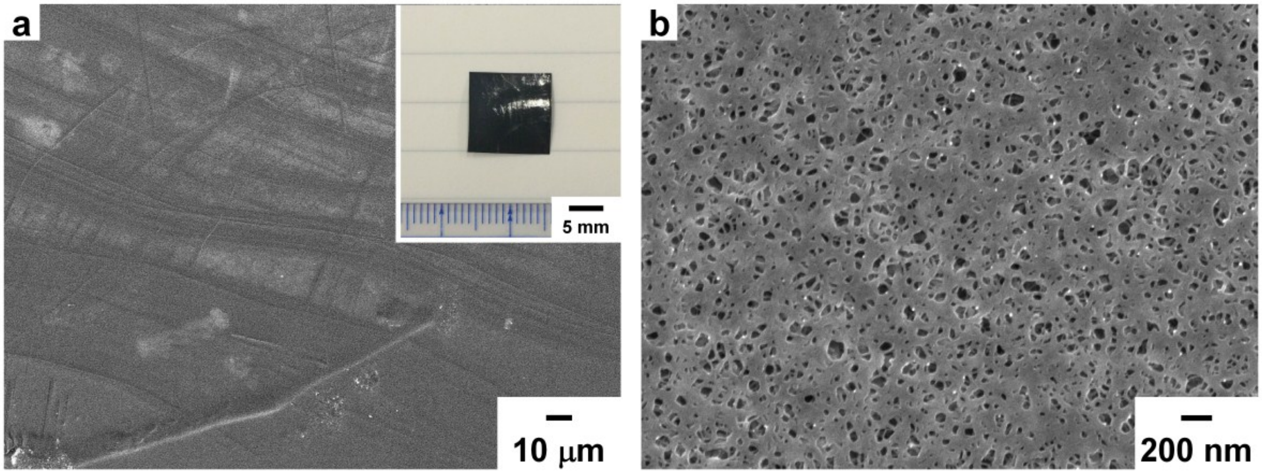


Fig. S17 (a,b) SEM images of the glass side of the PA film carbonized at 1100 °C. The inset shows a photograph of the glass side of the carbon film.

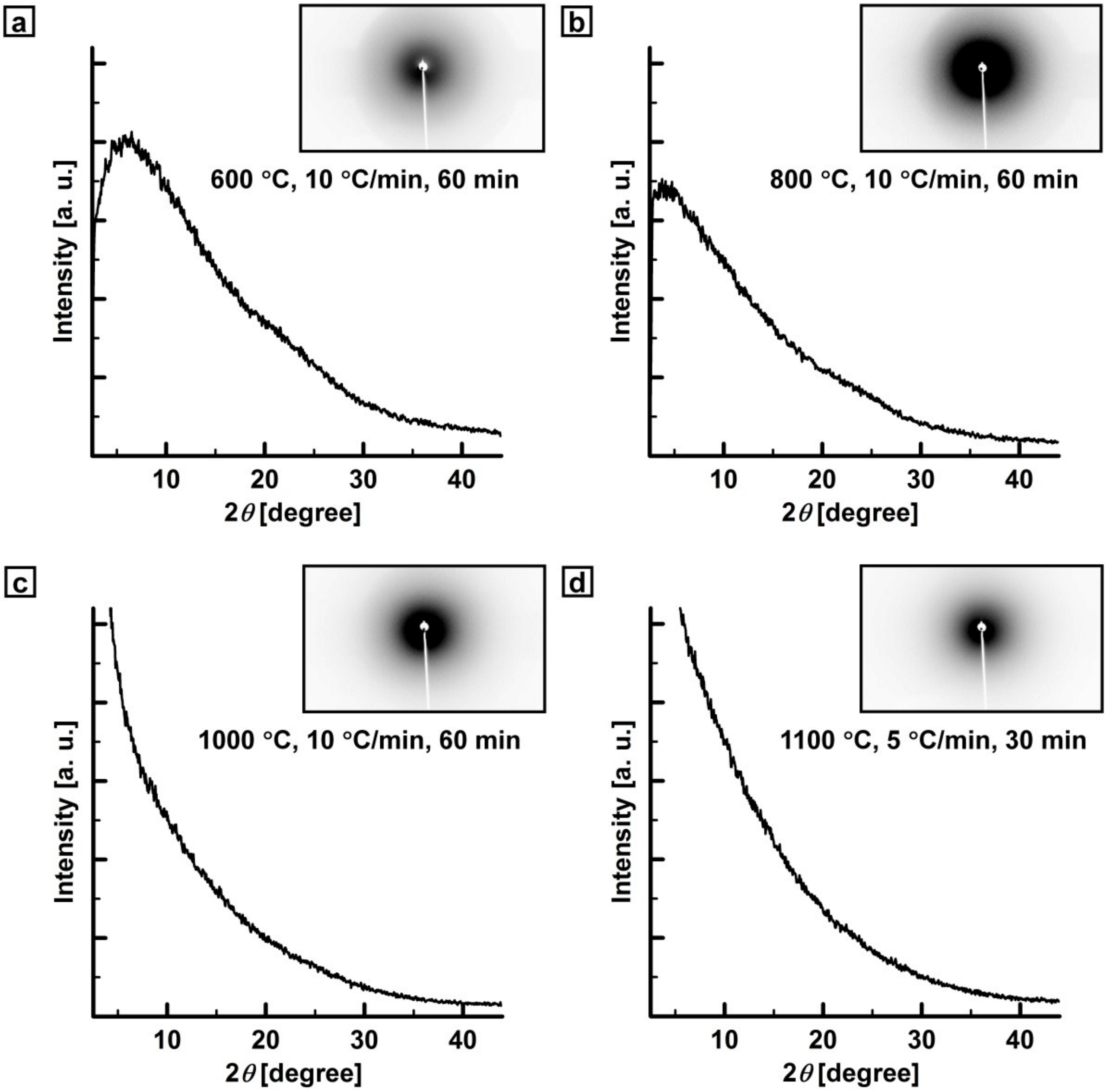


Fig. S18 XRD patterns of the PEDOT-based carbonaceous films prepared at (a) 600, (b) 800, (c) 1000, and (d) 1100 °C.

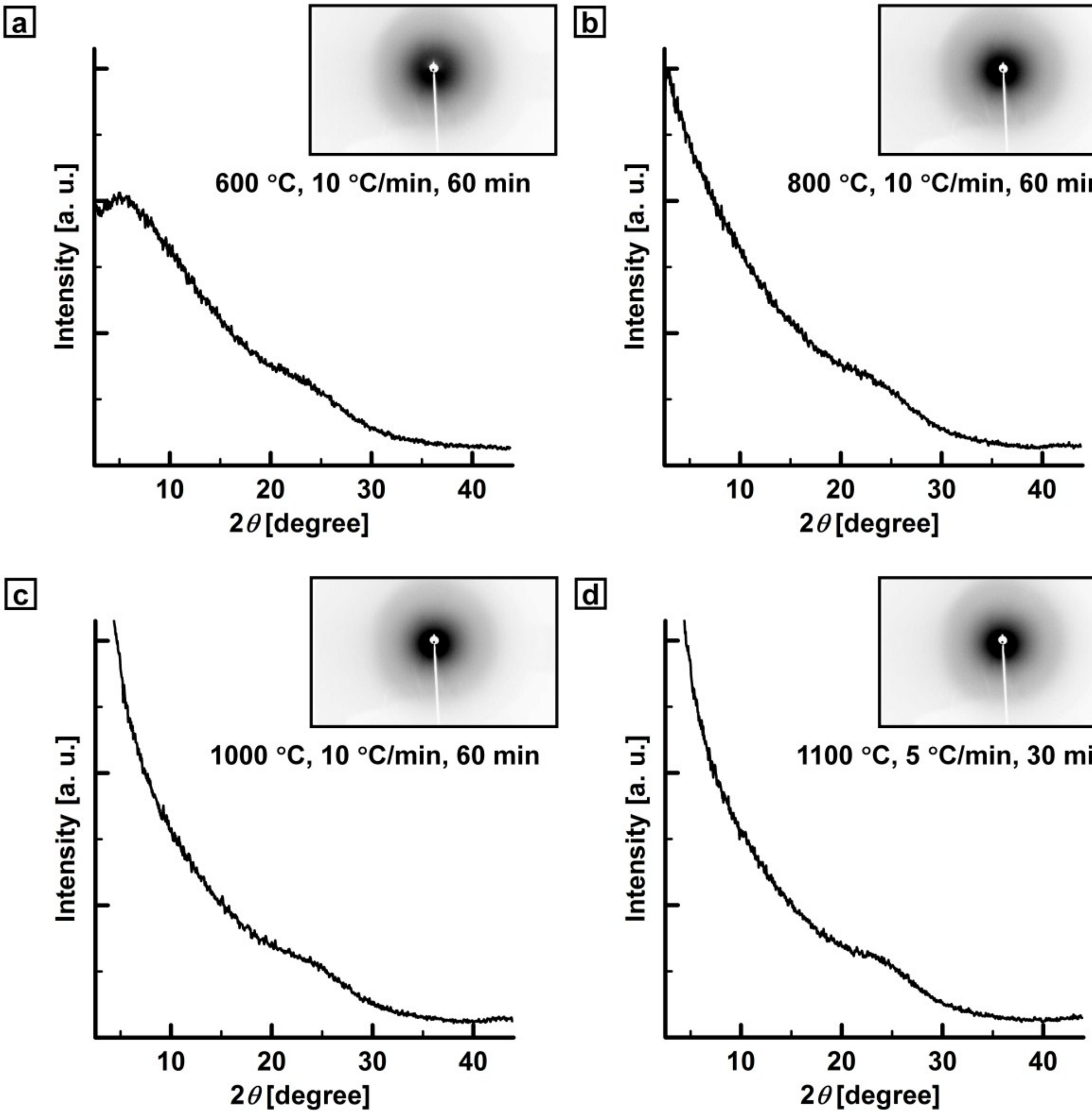


Fig. S19 XRD patterns of the PA-based carbon films prepared at (a) 600, (b) 800, (c) 1000, and (d) 1100 °C.

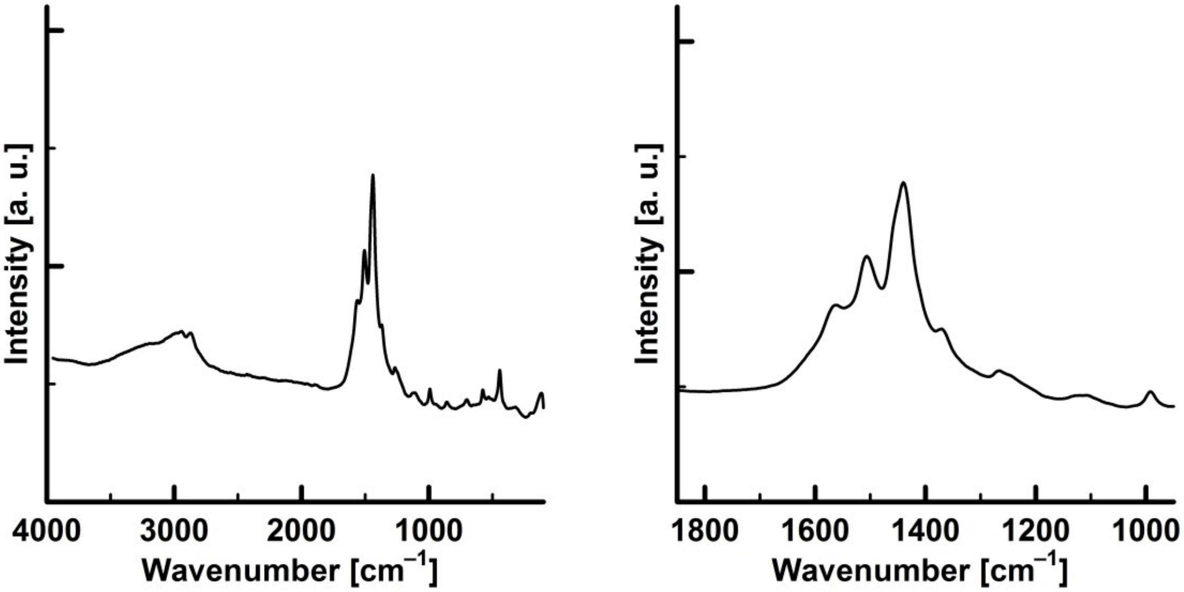


Fig. S20 Raman scattering spectra of the PEDOT film. The Raman spectrum had bands at 1562, 1506, 1440, and 1370 cm^{-1}, which were assigned to the asymmetric C_α=C_β stretching vibration (1562, 1506 cm^{-1}), symmetric C_α=C_β stretching vibration (1440 cm^{-1}), and C_β=C_β stretching vibration (1370 cm^{-1}).[8,9]

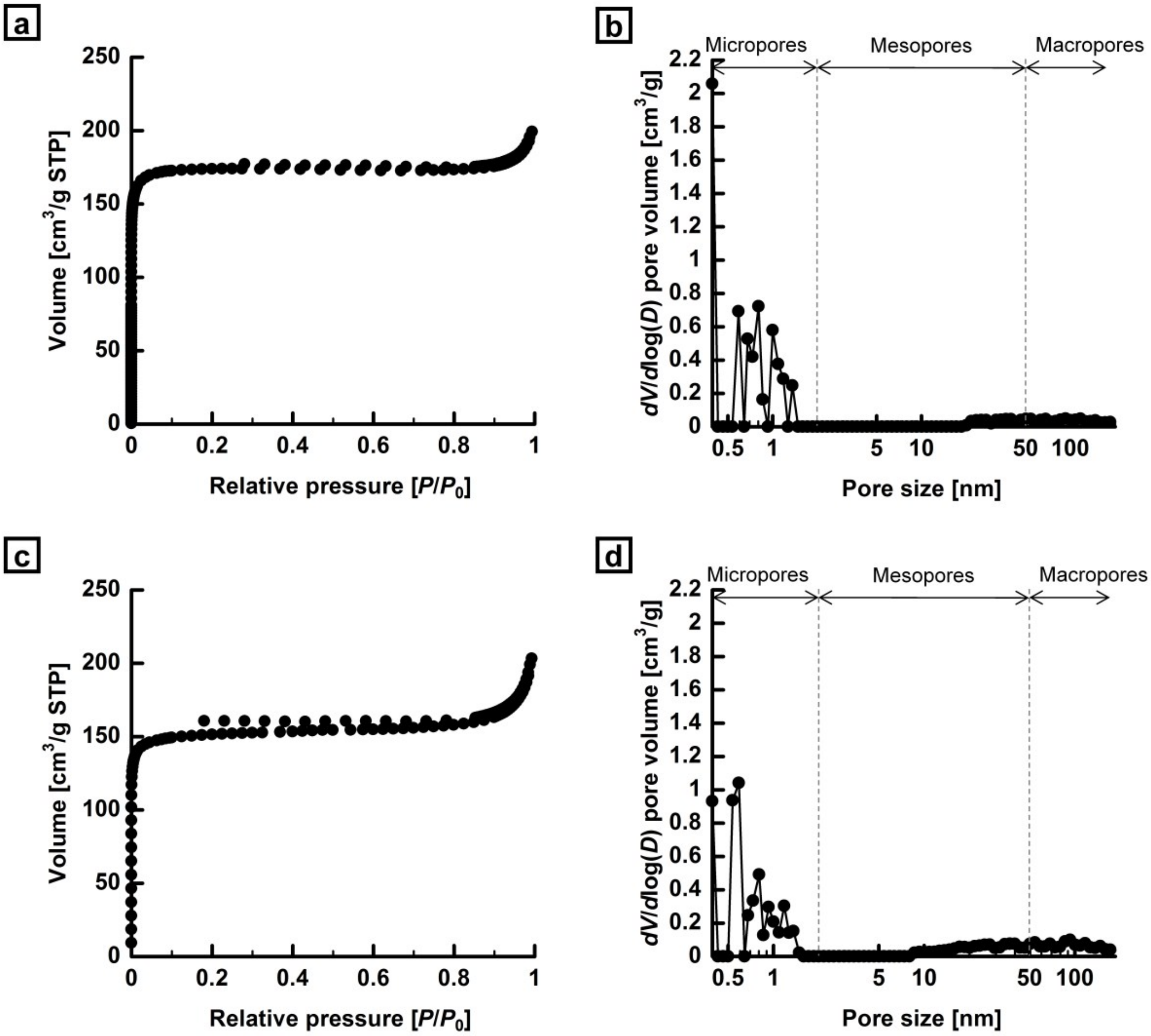


Fig. S21 (a,c) Nitrogen adsorption/desorption isotherms and (b,d) pore size distributions of the PEDOT-based carbonaceous films prepared at (a,b) 1000 and (c,d) 1100 °C.

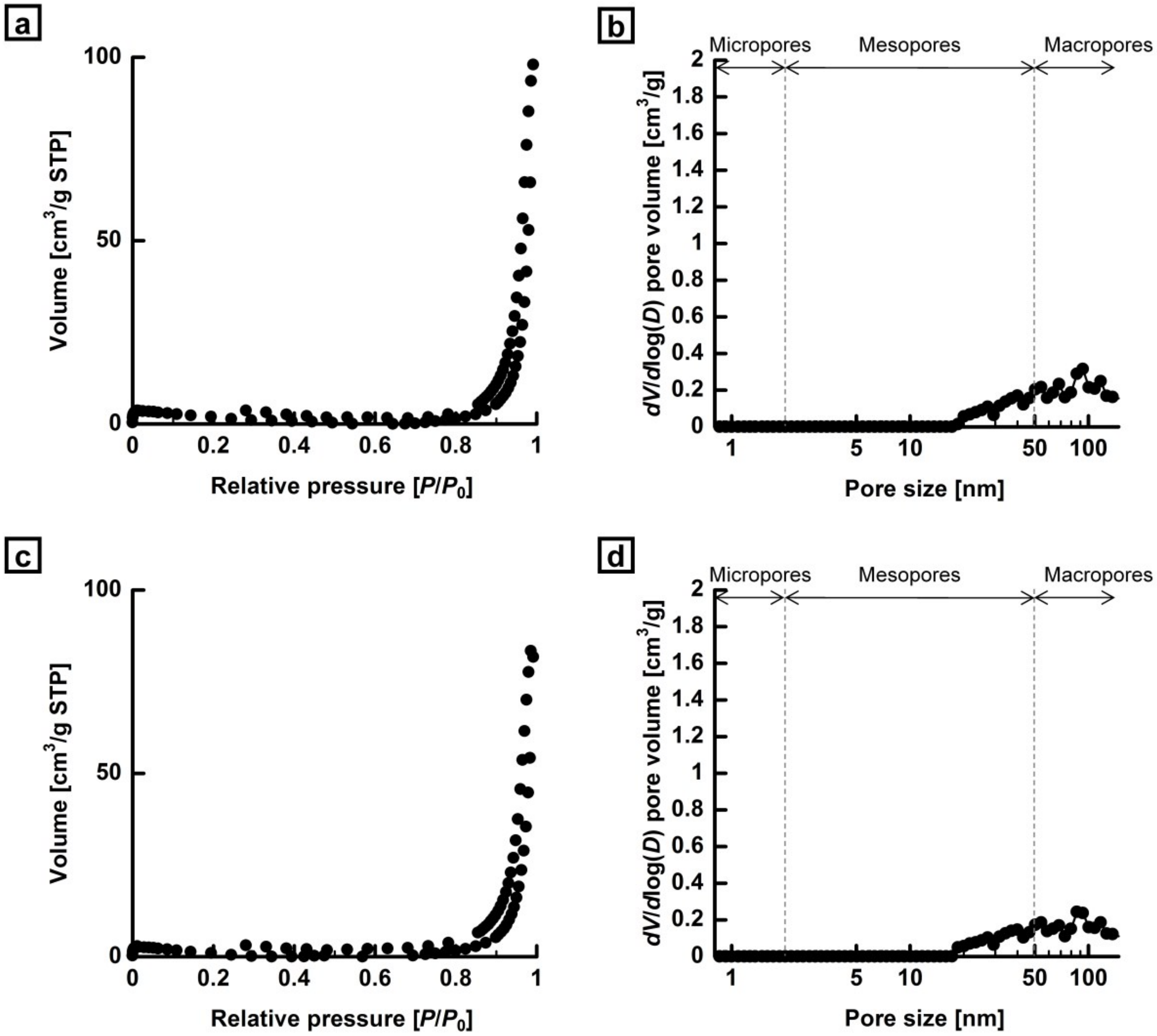


Fig. S22 (a,c) Nitrogen adsorption/desorption isotherms and (b,d) pore size distributions of the PA-based carbon films prepared at (a,b) 1000 and (c,d) 1100 °C.

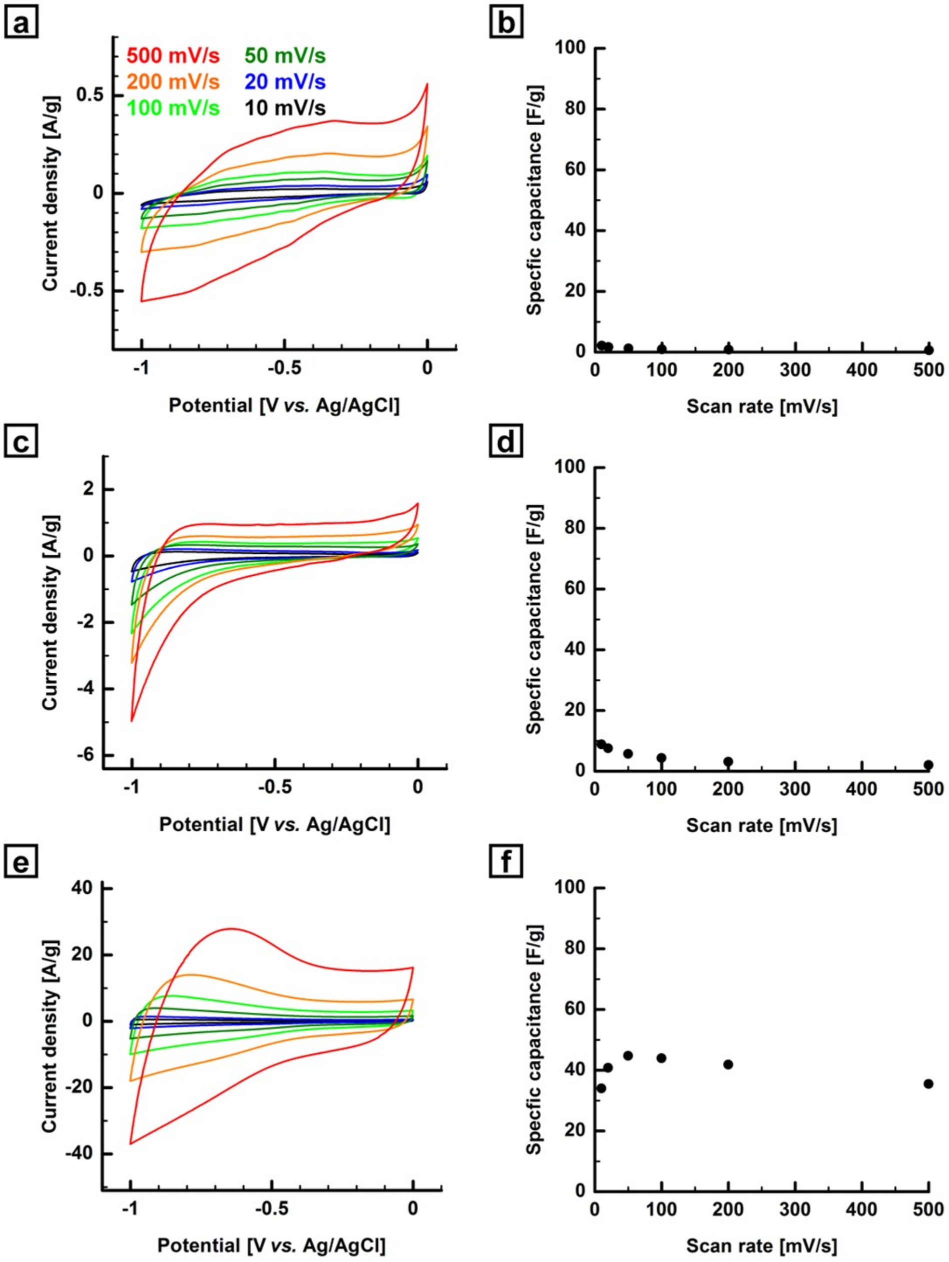


Fig. S23 Cyclic voltammograms of the PEDOT-based carbonaceous films prepared at (a) 600, (c) 800, and (e) 1000 °C at various scan rates in 5 M KCl aq. Relationship between specific capacitance and scan rate based on the CV curves of the carbonaceous films prepared at (b) 600, (d) 800, and (f) 1000 °C.

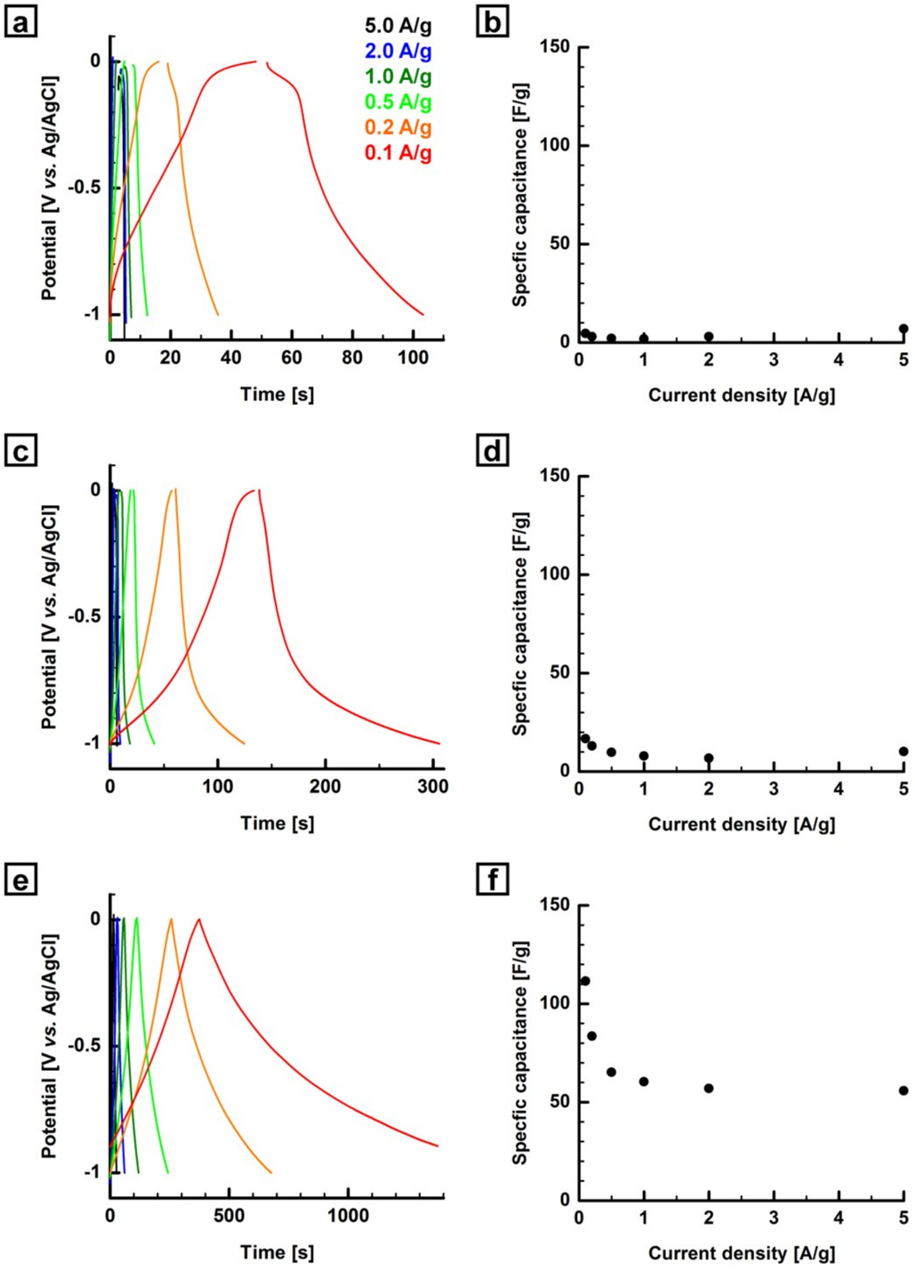


Fig. S24 GCD curves of the PEDOT-based carbonaceous films prepared at (a) 600, (c) 800, and (e) 1000 °C at various current densities in 5 M KCl aq. Relationship between specific capacitance and current density based on the GCD curves of the carbonaceous films prepared at (b) 600, (d) 800, and (f) 1000 °C (potential range: −1.0–0.0 V *vs.* Ag/AgCl).

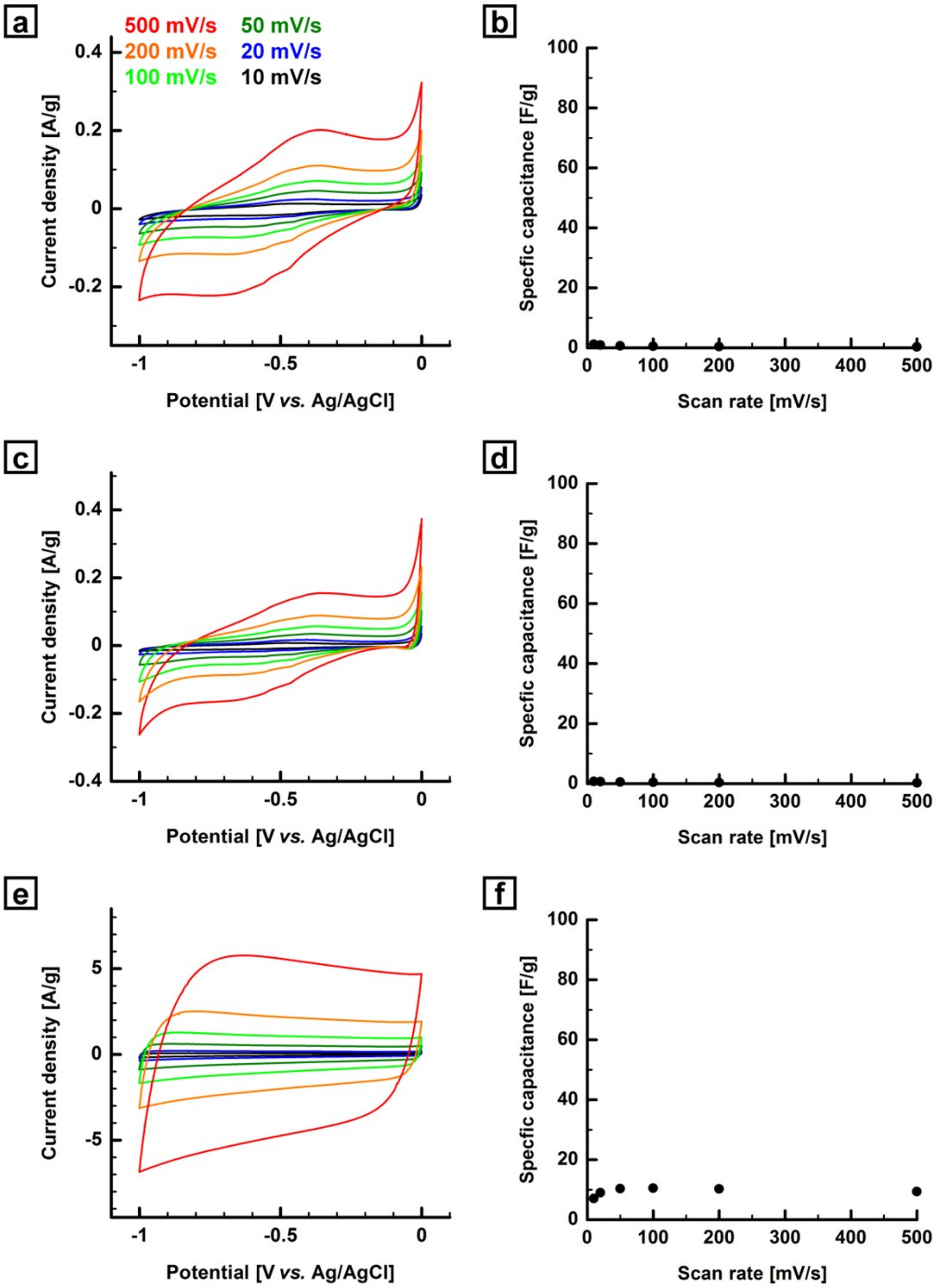


Fig. S25 Cyclic voltammograms of the PA-based carbon films prepared at (a) 600, (c) 800, and (e) 1000 °C at various scan rates in 5 M KCl aq. Relationship between specific capacitance and scan rate based on the cyclic voltammograms of the carbon films prepared at (b) 600, (d) 800, and (f) 1000 °C.

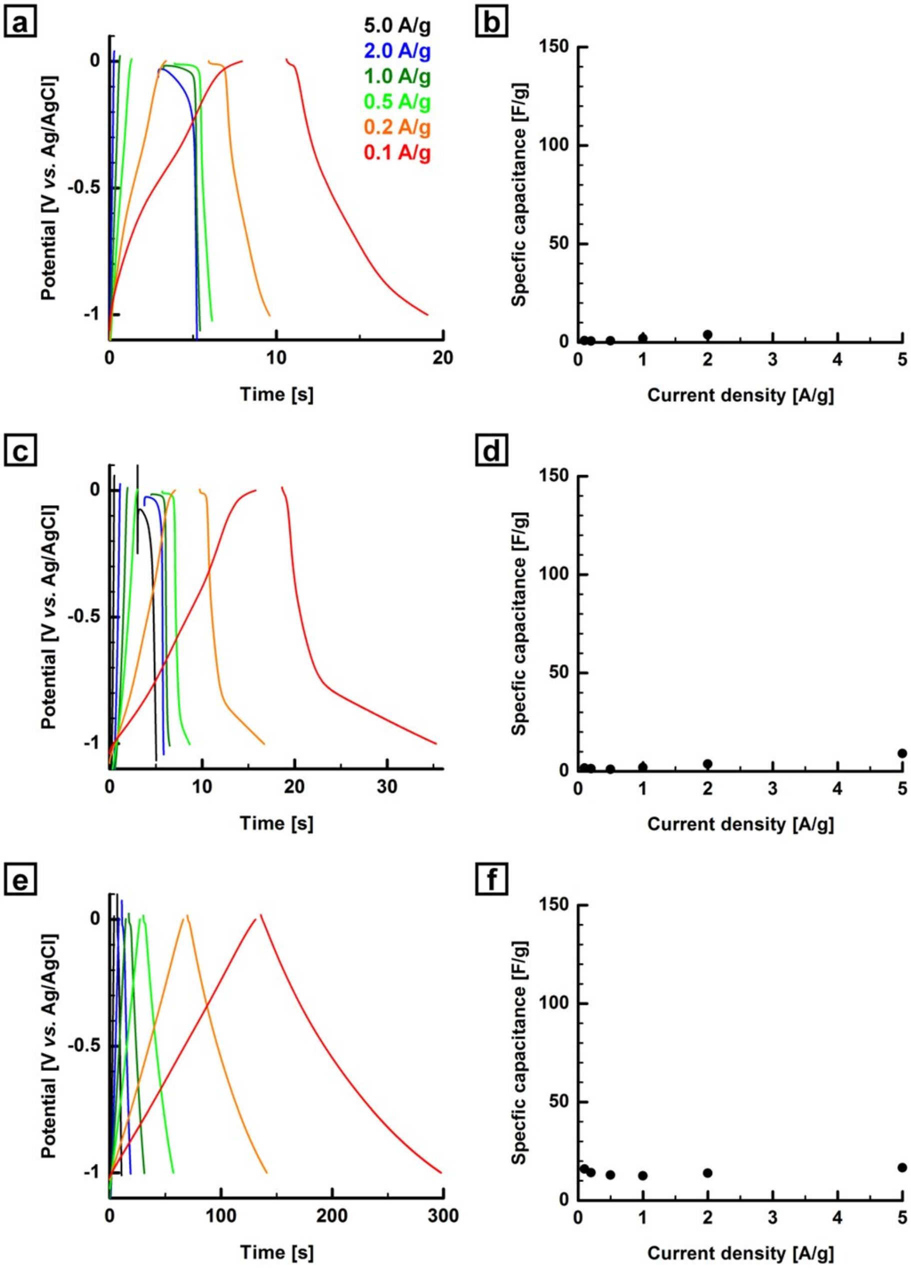


Fig. S26 GCD curves of the PA-based carbon films prepared at (a) 600, (c) 800, and (e) 1000 °C at various current densities in 5 M KCl aq. Relationship between specific capacitance and current density based on the GCD curves of the carbon films prepared at (b) 600, (d) 800, and (f) 1000 °C (potential range: −1.0–0.0 V *vs.* Ag/AgCl).

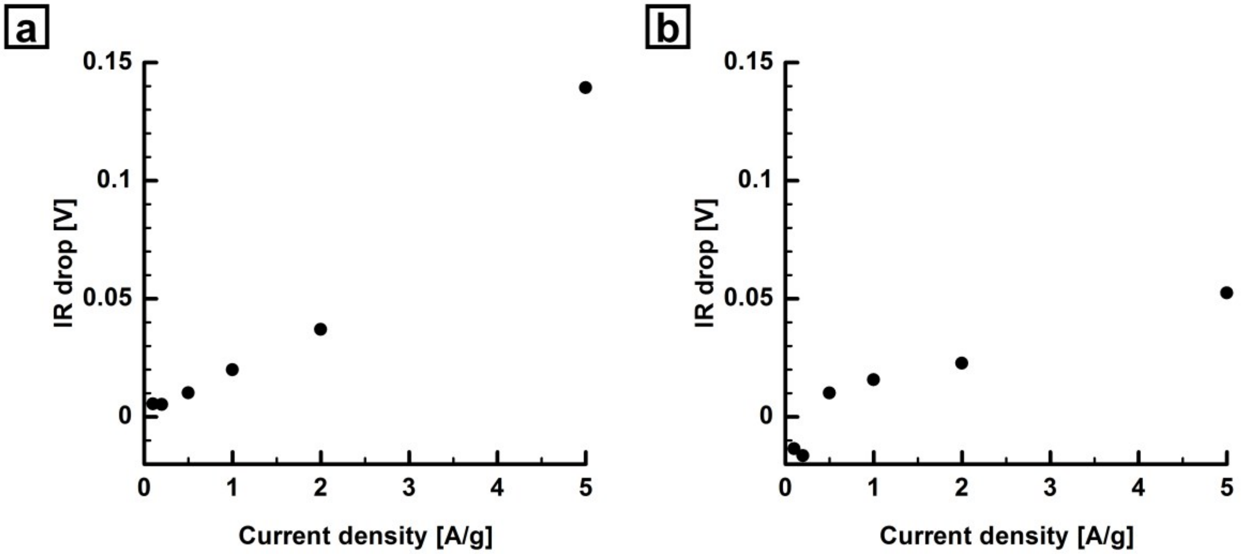


Fig. S27 Relationship between IR drop and current density based on the GCD curves of the carbon films prepared at 1100 °C using (a) PEDOT and (b) PA films.

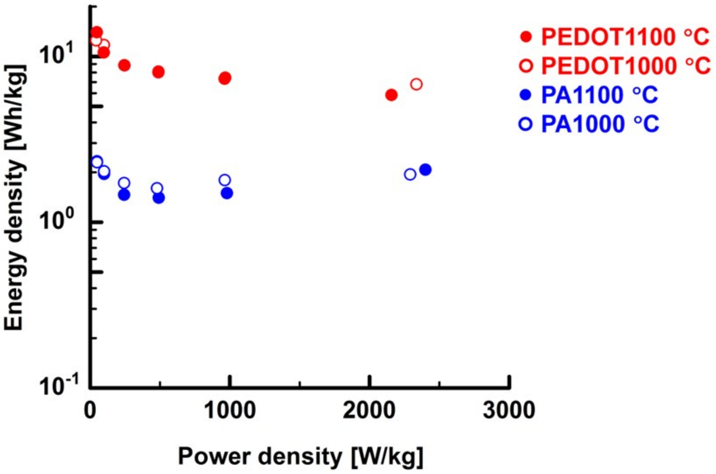


Fig. S28 Ragone plot for the carbonaceous film electrodes prepared at 1000–1100 °C.

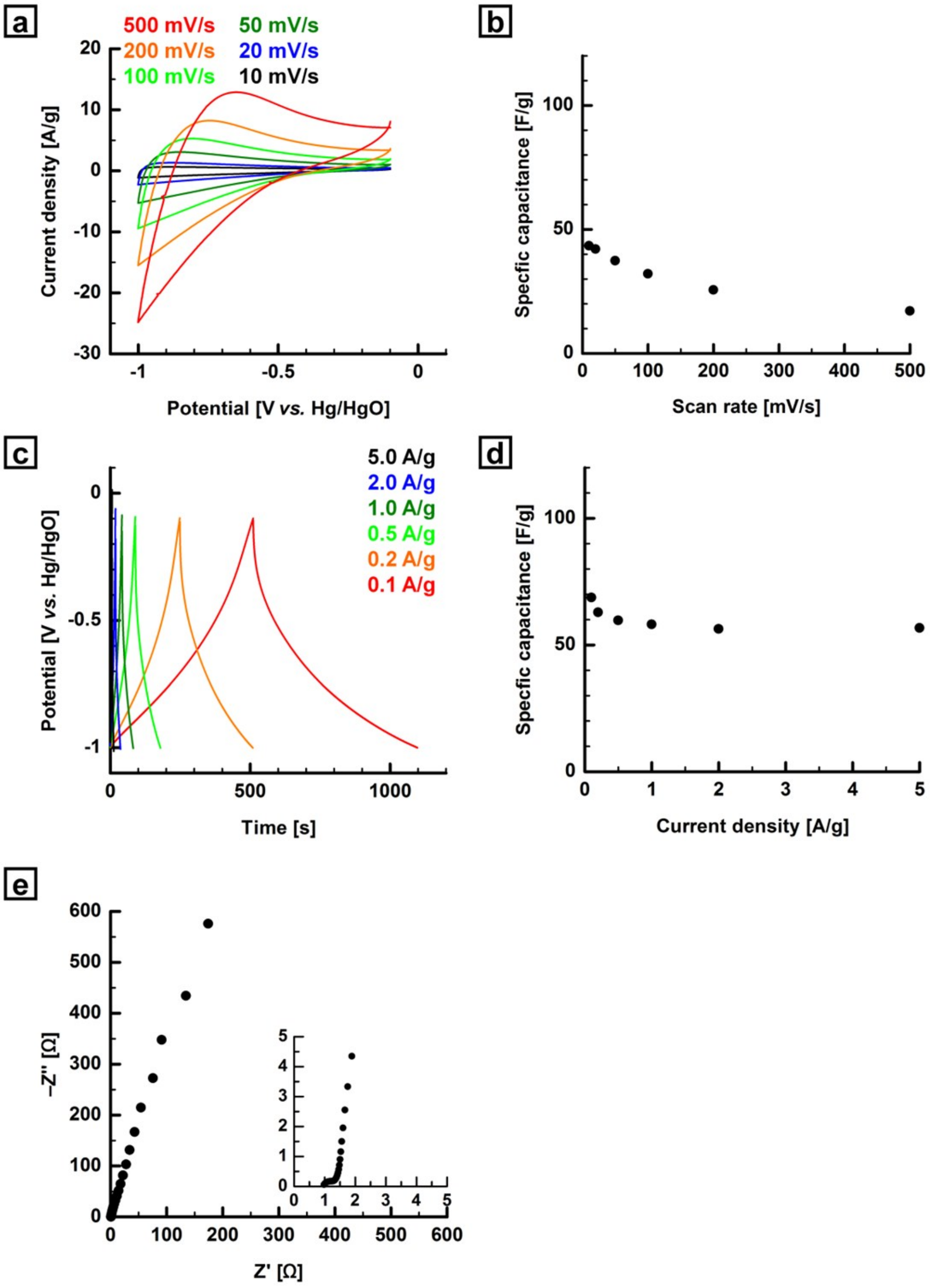


Fig. S29 (a) Cyclic voltammograms of the PEDOT-based carbonaceous film prepared at 1000 °C at various scan rates in 4 M KOH aq. (b) Relationship between specific capacitance and scan rate based on the cyclic voltammograms. (c) GCD curves of the PEDOT-based carbonaceous film prepared at 1000 °C at various current densities in 4 M KOH aq. (d) Relationship between specific capacitance and current density based on the GCD curves (potential range: −1.0–(−0.1) V *vs.* Hg/HgO). (e) Nyquist plot for the PEDOT-based carbonaceous film prepared at 1100 °C. The inset is a magnification of the plot. The equivalent series resistance (ESR) was estimated from the *x*-intercept of the Nyquist plot to be 0.9 Ω. A nearly vertical line was observed in low frequency region, indicating a pristine capacitive behavior.

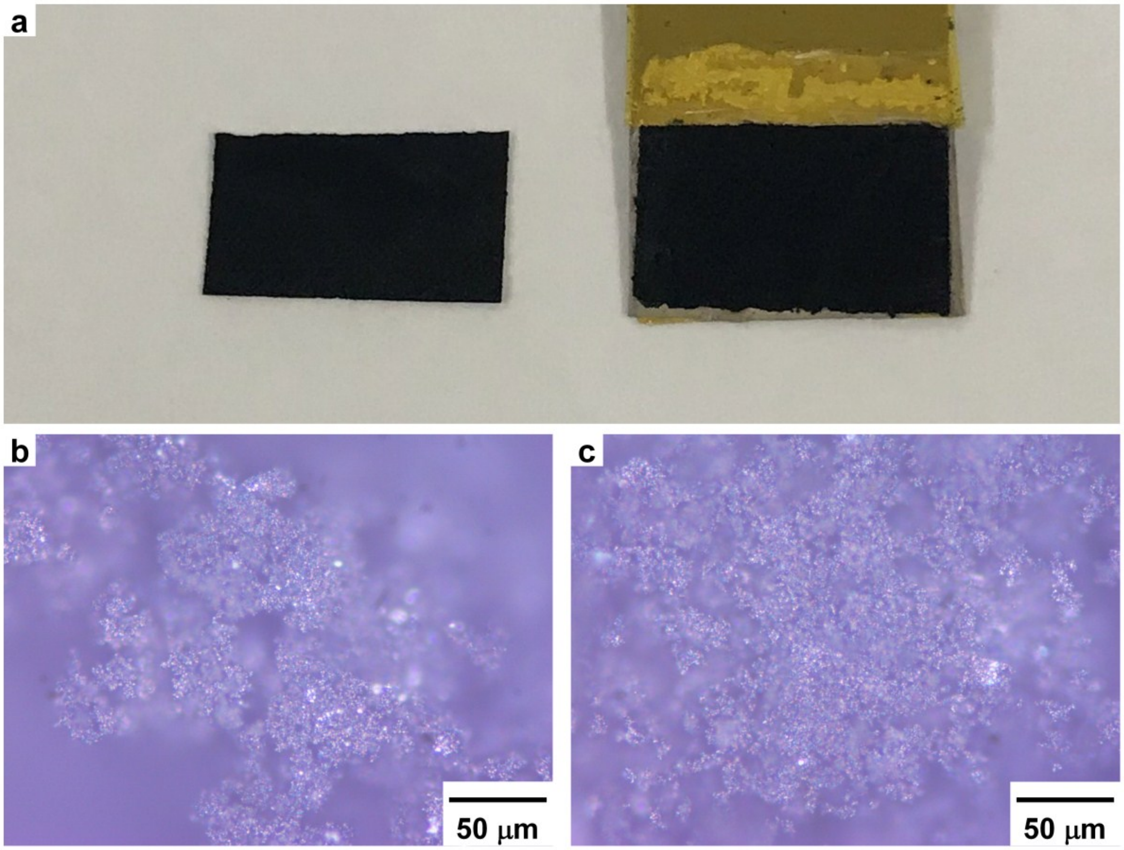
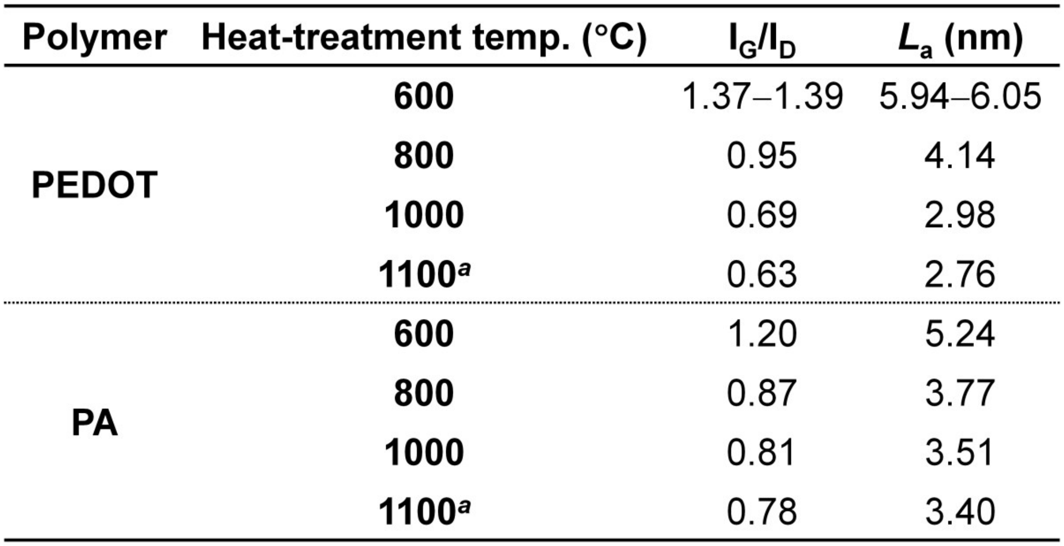


Fig. S30 (a) A photograph of the solution side of the PEDOT-based carbonaceous films before (left) and after (right) cycles (200th). Optical microscopy images of the carbonaceous films (b) before and (c) after cycles. No obvious sample damage was observed during the cyclability test.

Table S1 Raman intensity ratios between G- and D-bands (I_G/I_D) and L_a of the carbonaceous films prepared from the PEDOT and PA films at various temperatures.



Polymer	Heat-treatment temp. (°C)	I_G/I_D	L_a (nm)
PEDOT	**600**	1.37–1.39	5.94–6.05
	800	0.95	4.14
	1000	0.69	2.98
	1100[a]	0.63	2.76
PA	**600**	1.20	5.24
	800	0.87	3.77
	1000	0.81	3.51
	1100[a]	0.78	3.40

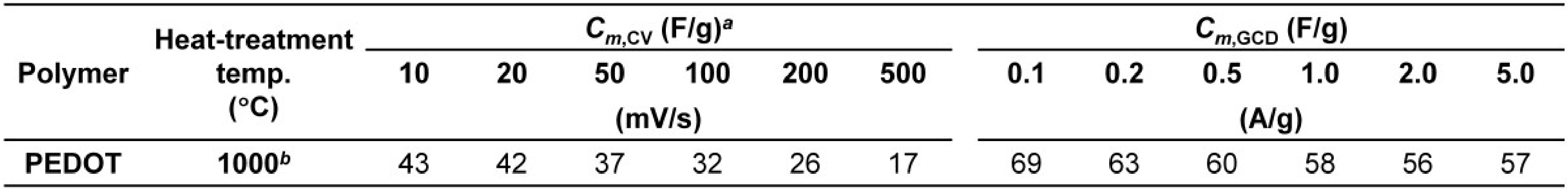
[a] The carbon film was prepared through a carbonization of a precursor polymer film at 600 °C for 30 min and the carbonized film was further heat treated at 1100 °C for 30 min with a heating rate of 5 °C/min.

Table S2 Summary of C_m values on the basis of the CV and GCD curves of the carbonaceous films prepared from the PEDOT and PA films at various temperatures in 5 M KCl aq.

Polymer	Heat-treatment temp. (°C)	$C_{m,\mathrm{CV}}$ (F/g)[a]						$C_{m,\mathrm{GCD}}$ (F/g)					
		10	20	50	100	200	500	0.1	0.2	0.5	1.0	2.0	5.0
		(mV/s)						(A/g)					
PEDOT	600	2.1	1.6	1.2	0.9	0.8	0.6	4.5	2.9	2.0	1.8	2.9	6.9
	800	8.8	7.5	5.7	4.4	3.1	2.0	17	13	9.7	7.9	6.8	10
	1000	34	41	45	44	42	35	111	84	65	60	57	56
	1100[b]	44	42	37	32	25	17	101	77	65	60	57	56
PA	600	1.1	0.9	0.6	0.5	0.4	0.3	0.8	0.6	0.7	1.9	3.8	–[c]
	800	0.7	0.6	0.5	0.4	0.3	0.2	1.6	1.3	1.0	1.9	3.7	9.0
	1000	7.0	9.0	10	10	10	9.3	16	14	13	12	14	17
	1100[b]	7.8	7.7	7.5	7.1	6.7	5.9	16	14	11	10	11	16

[a] Potential range: −1.0–0.0 V or −1.0–(−0.1) V *vs.* Ag/AgCl. [b] The carbon film was prepared through a carbonization of a precursor polymer film at 600 °C for 30 min and the carbonized film was further heat treated at 1100 °C for 30 min with a heating rate of 5 °C/min. [c] Data not available.

Table S3 Summary of C_m values on the basis of the cyclic voltammograms and GCD curves of the PEDOT-based carbonaceous film prepared at 1000 °C in 4 M KOH aq.



Polymer	Heat-treatment temp. (°C)	$C_{m,\mathrm{CV}}$ (F/g)[a]						$C_{m,\mathrm{GCD}}$ (F/g)					
		10	20	50	100	200	500	0.1	0.2	0.5	1.0	2.0	5.0
		(mV/s)						(A/g)					
PEDOT	**1000**[b]	43	42	37	32	26	17	69	63	60	58	56	57

[a] Potential range: −1.0–(−0.1) V *vs.* Hg/HgO. [b] The carbonaceous film was prepared through a carbonization of a PEDOT film at 1000 °C for 3 h with a heating rate of 10 °C/min.