Development of highly conductive PEDOT system by doping with partially crystalline sulfated cellulose and their electric conductivity

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Using direct sulfation of cellulose, we prepared sulfated cellulose (CS) with various degrees of substitution of sulfate groups (DS), which we used as dopants for PEDOT. PEDOT/CS were prepared via in situ chemical oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) in an aqueous CS solution. Films of the obtained PEDOT/CS were formed using spin-coating. As a reference, a PEDOT/PSS film was also formed. The electrical conductivity of the PEDOT/CS film with a DS of 1.03 was 0.576 S m^{-1}. In contrast, the electrical conductivity of the PEDOT/PSS film was 0.0153 S cm^{-1}. Using Raman spectroscopy, we found that the 1400 and 1500 cm^{-1} bands correspond to $C_\alpha = C_\beta$ vibrations in the five-member PEDOT ring. Compared with the band of the PEDOT/PSS film, the band of the PEDOT/CS film red-shifted from 1437 to 1433 cm^{-1} and narrowed. We attributed the increased electrical conductivity of the PEDOT/CS film to a greater proportion of the quinoid structure than in PEDOT contained in PEDOT/PSS.

Introduction

Many kinds of conductive polymers such as polyaniline, polypyrroles, polythiophenes, and polyphenylenes have been developed to replace indium tin oxide (ITO).[1-4] Because it has the highest conductivity of these conductive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is especially interesting. PEDOT-based polymers are used in many fields, such as in inorganic electroluminescent devices, touch panels, rechargeable batteries, and photovoltaic devices.[5-8]

Recently, researchers have found that the conductivity of poly(3,4-ethylenedioxythiophene)/polystyrenesulfonate (PEDOT/PSS) films are enhanced by adding polar organic compounds, such as glycol or sorbitol, to the PEDOT/PSS aqueous solution.[9-12] For example, Okuzaki et al. increased the electrical conductivity of the solid film by two orders of magnitude (600 S cm^{-1}) by using the polar groups in glycol or sorbitol.[12] The single crystallization of PEDOT was assisted by ethylene glycol (EG) as a secondary dopant. Ouyang et al. attributed this behavior to the PEDOT chain transforming from benzoid to quinoid structure, because PEDOT co-exists with polar groups such as hydroxyl groups. They confirmed that the conductivity of the PEDOT/PSS film was enhanced from 0.4 to 200 S cm^{-1} by adding EG into the PEDOT/PSS aqueous solution. They proposed that the driving force for their transformation of structure was the interaction between the dipole of one polar group of organic compound and dipoles or positive charges on the PEDOT chains.[13] These composites have also been studied from another perspective. Recently, Mengistie et al. reported producing a PEDOT/PSS film with high conductivity, 1200 S cm^{-1}, by treating its surface with formic acid, a polar compound. They explained that formic acid treatment with a high dielectric constant screens the Coulombic attraction between the PEDOT and PSS chains, leading to phase separation between them, generating PEDOT chains that are linearly oriented and interconnected.[14] Also, Zhang et al. reported the properties of conductive polymer–polysaccharide composite films, focusing on polysaccharides as biodegradable, biocompatible materials.[15]

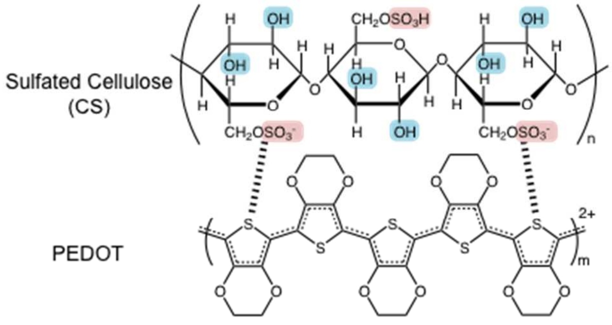


Fig. 1 Structure of PEDOT/CS.

Using electropolymerization, they prepared several kinds of PEDOT films, doping them with polysaccharides such as carboxymethyl cellulose, hyaluronic acid, xanthan gum, pectin, and gellan gum, and then examined the electrochemical properties, morphology, and other properties of the films.[15]

We focused on sulfated polysaccharides with hydroxyl groups as dopants and adopted cellulose with rigid chains of linear β (1→4)-linked glucopyranose residues,[16] because PEDOT molecules are presumed to line around the cellulose rigid chains and be easy to crystallize. In this paper, using direct sulfation of cellulose we prepared sulfated cellulose (CS) with various degrees of substitution of sulfate groups (DS), which we used as PEDOT dopants. After preparing the dopants, we prepared PEDOT films doped with a series of CS samples (Fig. 1) by chemical oxidative polymerization. Once we formed the films, we analyzed and discussed their electrochemical properties and surface morphologies as a function of the DS of CS. Thus, we present a new approach for highly conductive PEDOT systems by doping with partially crystalline sulfated cellulose.

Experimental

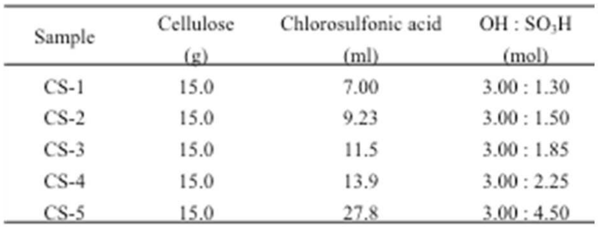
Materials

Cellulose powder, used as a starting material, was purchased from Sigma-Aldrich Japan Co. LLC (Tokyo, Japan). The cellulose was sulfated using chlorosulfonic acid (Sigma-Aldrich Japan Co. LLC). 3,4-Ethylenedioxythiophene (EDOT) (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) was used for the monomer of PEDOT. Potassium persulfate, used as a radical initiator, was purchased from Nacalai Tesque, Inc. (Tokyo, Japan). Iron(III) sulfate *n*-hydrate (Wako Chemicals Co. Ltd., Tokyo, Japan) was used as a redox reagent. PEDOT/PSS (conductive grade PEDOT/PSS, from commercial product catalogue), used as a reference conductive polymer, was purchased from Sigma-Aldrich Japan Co. LLC.

Measurement

The molecular weights of the CS samples were measured by size exclusion chromatography (SEC) (JASCO Corp., Tokyo, Japan) using an SEC packed column with an exclusion molecular weight (M_W) of 2.0 × 10^7 (Shodex OHpack SB-806M HQ, 300 × 8.0 mm I.D., Showa Denko K. K., Tokyo, Japan). The SEC calibration curve was made from the elution times of pullulan standards (M_W = 0.58 × 10^4, 1.22 × 10^4, 2.37 × 10^4, 4.80 × 10^4, 10.0 × 10^4, 18.6 × 10^4, 38.0 × 10^4, and 85.3 × 10^4) (Shodex Standard P-82, Showa Denko K. K.). Conductivity was evaluated by measuring sheet resistance via the four-terminal method using a resistance meter (Loresta-GP or Hiresta-UP, Mitsubishi Chemical Analytech Co. Ltd., Tokyo, Japan). Raman spectra were measured using a laser Raman spectrophotometer (NRS-5100, JASCO Corp.). The transparencies of the PEDOT thin films were evaluated using UV-visible absorption spectrometer (UV-VIS 560, JASCO Corp.). The surface morphologies of the PEDOT thin films were observed using a scanning probe microscope (SPM) (Dimension Icon-ES1001 SPM System, Veeco Instruments Inc., Plainview, NY USA). The DS of the sulfate group was estimated from the sulfur content, measured by elemental analysis (vario MICRO cube, Elementar Analysensysteme, Frankfurt, Germany) of the sulfated cellulose. The particle size and distribution of PEDOT in the aqueous dispersion were measured using dynamic light scattering (DLS) (Zatasizer Nano ZS, Malvern Instruments Ltd., Malvern, UK). Fourier transform-infrared (FT-IR) spectra of the CS samples were also collected (FT/IR-6300, JASCO Corp.). Geometry optimization and normal mode analysis were performed for glucose and sulfated glucose as model compounds using the B3LYP hybrid density functional method. 6-31G(d) was used as the basis set of H, C, and O atoms, and Lanl2DZdp was adopted for S atoms. 6-31G(d) and Lanl2DZdp were performed using GAMESS software. The crystallinities of the CS samples were assessed using X-ray diffraction (SmartLab, Rigaku Corp, Tokyo, Japan). The thicknesses of the PEDOT thin films were measured using a stylus profilometer (Dektak-150, Bruker Corp, Tucson, AZ, USA).

Table 1 Preparation condition of CS



Sample	Cellulose (g)	Chlorosulfonic acid (ml)	OH : SO_3H (mol)
CS-1	15.0	7.00	3.00 : 1.30
CS-2	15.0	9.23	3.00 : 1.50
CS-3	15.0	11.5	3.00 : 1.85
CS-4	15.0	13.9	3.00 : 2.25
CS-5	15.0	27.8	3.00 : 4.50

Preparation of CS

First, 15.0 g of cellulose powder was suspended in 750 mL of *N,N*-dimethylformamide (DMF) and stirred for 14 h. After heating to 50 ˚C, a varying amount of chlorosulfonic acid (1.30, 1.50, 1.85, 2.25 and 4.5 eq. of glucose unit of cellulose) was gradually dropped into the cellulose/DMF dispersion over 30 min and the mixture was then stirred for 5 h, as summarized in Table 1. The product mixtures were then reprecipitated using a saturated sodium acetate-ethanol solution and washed three times using the same solution. The supernatant was washed using ethanol until its pH became 7.0. The precipitate was dissolved in water and was purified by dialysis using molecular-scale porous membrane tubing with a cut-off molecular weight (MWCO) of 3500 (Spectra/por3, Spectrum Laboratories Inc., Rancho Dominguez, CA, USA) for 72 h. The obtained products were then freeze-dried.

Preparation of PEDOT/CS

PEDOT/CS was prepared by polymerization of EDOT in an aqueous solution of sodium cellulose sulfate salt. 0.20 g of CS-1, -2, -3, -4, or -5 was dissolved in 20 ml of water. First, 0.20 g of CS-1, -2, -3, -4, or -5 was dissolved in 20 mL of water and concentrated hydrochloric acid was added to acidify the CS aqueous solution. Next, 0.20 g of EDOT was added to the acidic CS aqueous solution and dispersed by sonication with an

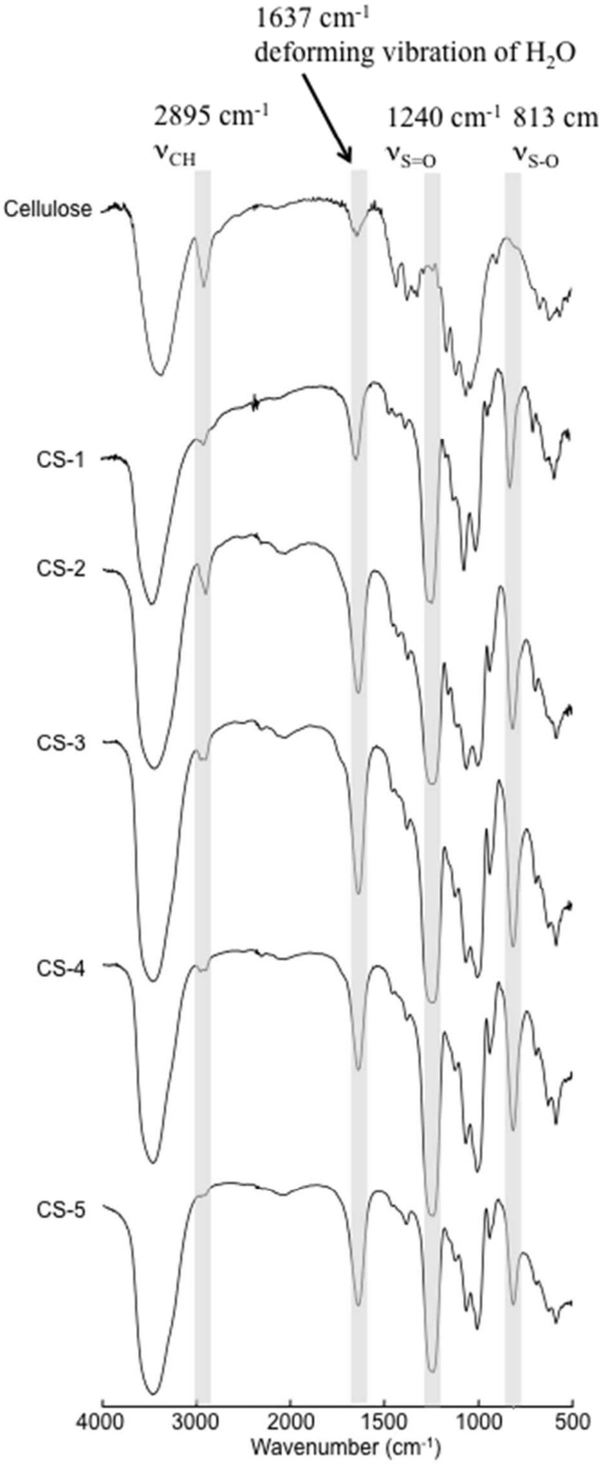


Fig. 2 FT-IR spectra of cellulose and CS.

ultrasonic probe. Then, 0.38 g of potassium persulfate, used as a radical initiator, was added to the dispersion with 1.4 mg of iron(III) sulfate *n*-hydrate, used as a redox reagent, and stirred for 1 day. The products were dialyzed using dialysis tubing (MWCO = 3500) for 72 h. Then, the concentration of the aqueous dispersion was increased to 0.6 wt% by evaporation.

Table 2 Elemental analysis, DS value and molecular weight

CS	C%	S%	DS value	$M_w \times 10^3$
CS-1	26.1	10.4	0.90	8.46
CS-2	25.8	11.8	1.03	9.76
CS-3	23.3	13.2	1.28	8.15
CS-4	20.8	14.2	1.53	10.0
CS-5	16.1	14.8	2.06	8.98

The concentration of the commercial PEDOT/PSS solution was also reduced from 1.3 to 0.6 wt%.

Fabrication of PEDOT/CS thin films

The PEDOT/CS films were formed on glass substrates by spin-coating with PEDOT/CS solutions, as reported by Crispin et al.[17] After the glass substrate was sonicated for 15 min in water, it was washed successively in acetone, water, and ethanol, dried, and then treated by UV ozone cleaning.

On glass substrates, 300 μl of the various PEDOT/CS H_2O dispersions (0.6 wt%) were spin-coated at 1000 rpm. These wet films of PEDOT/CS were heated at 120°C for 20 min. This procedure from spin-coating to heating was repeated three times, producing transparent PEDOT/CS films. As a reference conductive polymer film, a transparent film was fabricated using the same process with a commercial PEDOT/PSS solution.

Results and Discussion

Characterization of CS

Figure 2 shows FT-IR spectra of cellulose and the CS-1, -2, -3, -4, and -5 samples. We attribute their main characteristic peaks to absorption by $\nu_{s=o}$ at 1240 cm^{-1} and $\nu_{s\text{–}o}$ at 813 cm^{-1}, which was not present in the IR spectrum of cellulose, as shown in Fig. 2. The peak near 1640 cm^{-1} is attributed to the deforming vibrations of H_2O. The more this peak's signal gradually increased, the more the DS value increased. This behavior indicated that the amount of H_2O adsorbed on cellulose molecules increased as the hydrophilic property of cellulose increased because of the introduction of sulfate groups. However, the peak near 2895 cm^{-1} is attributed to stretching vibrations of CH-bonded sulfate groups. This peak's signal weakened gradually as sulfate groups were introduced. It was suggested that the stretching vibrations band of the CH bond of the 6- or 2-*O* position of the glucose unit substituted by sulfate groups, regioselectively, were reduced by the electron-attractive property of the sulfate group. The phenomenon of the decreasing stretching vibrations of the CH bond was demonstrated using the B3LYP hybrid density functional method.

Table 2 summarizes the elemental analysis of CS and their DS estimated from their sulfur contents. These results confirm that the DS increased gradually with increases in the adding ratio of chlorosulfonic acid during sulfation of cellulose. The estimated DS values of the CS-1, -2, -3, -4, and -5 samples were 0.9, 1.03, 1.28, 1.53, and 2.06, respectively. The average M_W values of the CS samples were determined by an SEC calibration curve using pullulan. Table 2 summarizes the M_W values of the CS samples. The average M_W values of the CS-1, -2, -3, -4, and -5 samples were 8×10^3~10.0×10^3 Da. The M_W distributions of the CS were broad. The sulfate group was primarily introduced to the 6-*O* position and then to the 2-*O* and 3-*O* positions, as reported by Zhang et al.[18] and Qin et al..[19] Therefore, CS-1 and -2 contain cellulose of which sulfate groups are introduced to the 6-*O* position.

Table 3 Zeta potential, Z average particle diameter and PDI of PEDOT/PSS and PEDOT/CS

PEDOT	Zeta potential (mV)	Z average (nm)	PDI
PEDOT/PSS	-73.8	977	0.455
PEDOT/CS-1	-39.9	330	0.472
PEDOT/CS-2	-40.3	264	0.355
PEDOT/CS-3	-40.9	343	0.391
PEDOT/CS-4	-47.5	331	0.237
PEDOT/CS-5	-36.2	281	0.144

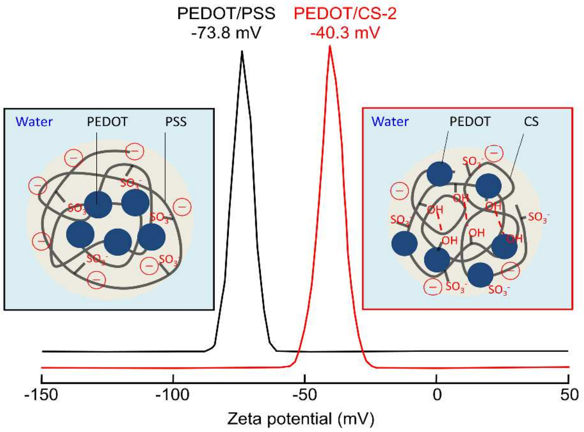


Fig. 3 Zeta potential distribution of PEDOT/PSS and PEDOT/CS-2.

Table 4 Thickness and their electric conductivity of PEDOT thin films

Sample	t (nm)	ρ x 10^{-6} (Ω/sq.)	σ x 10^{-3} (S cm^{-1})
PEDOT/PSS	74	8.77	15.3
PEDOT/CS-1	79	0.29	436
PEDOT/CS-2	59	0.25	576
PEDOT/CS-3	44	0.90	253
PEDOT/CS-4	53	13.1	14.0
PEDOT/CS-5	32	21500	0.014

Characterization of PEDOT/CS particles

Table 3 summarizes the zeta potential, Z average, and their polydispersity index (PDI) of PEDOT/PSS and PEDOT/CS particles in H_2O. The PEDOT/PSS particles had a zeta potential of -73.8 mV, but all kinds of PEDOT/CS particles had values around -40 mV. These results indicate that the surfaces of the PEDOT/PSS particles were rich in sulfonyl groups, as shown in Fig. 3.

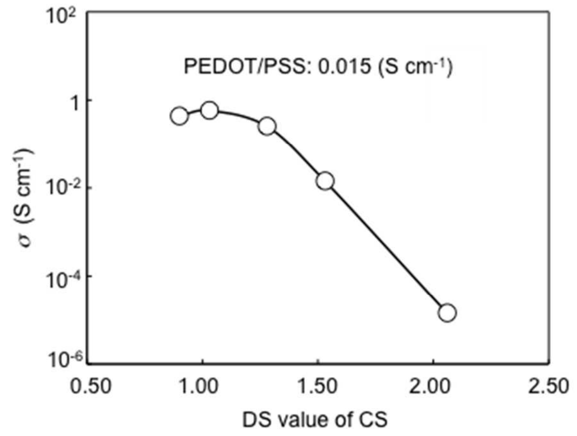


Fig. 4 Relationship between electrical conductivity and the degree of substitution of sulfuric groups.

On the other hand, Z average particle diameters and PDIs for the PEDOT/PSS and PEDOT/CS particles in H_2O, determined by DLS. The Z average particle diameter of the PEDOT/CS particles ranged from about 250 to 350 nm. The DLS data of PEDOT/PSS particles dispersions in H_2O and H_2O/ethanol mixed solution were provided as Fig. S1.

Characterization of PEDOT/CS thin films

Using the four-terminal method, we measured the surface resistances of five thin films fabricated using the obtained PEDOT/CS particles. To estimate their volume resistance and electrical conductivity, we measured their thickness using a stylus profilometer.

Table 4 summarizes the surface resistance and film thickness of these samples, as well as the volume resistance and electrical conductivity of the PEDOT thin films estimated from Eq. 1.

$$\sigma = \frac{1}{\rho_s \times t} \qquad \text{Eq. 1}$$

We evaluated the PEDOT/PSS film as a reference using the same method as summarized in Table 4. The film thickness of PEDOT/CS was ca. 30 - 80 nm. The electrical conductivity depended slightly on film thickness. We tried to fabricate thicker PEDOT/CS films, as summarized in Table S1, and compared two series of PEDOT/CS films with different film thicknesses. The details of the film behavior and thickness

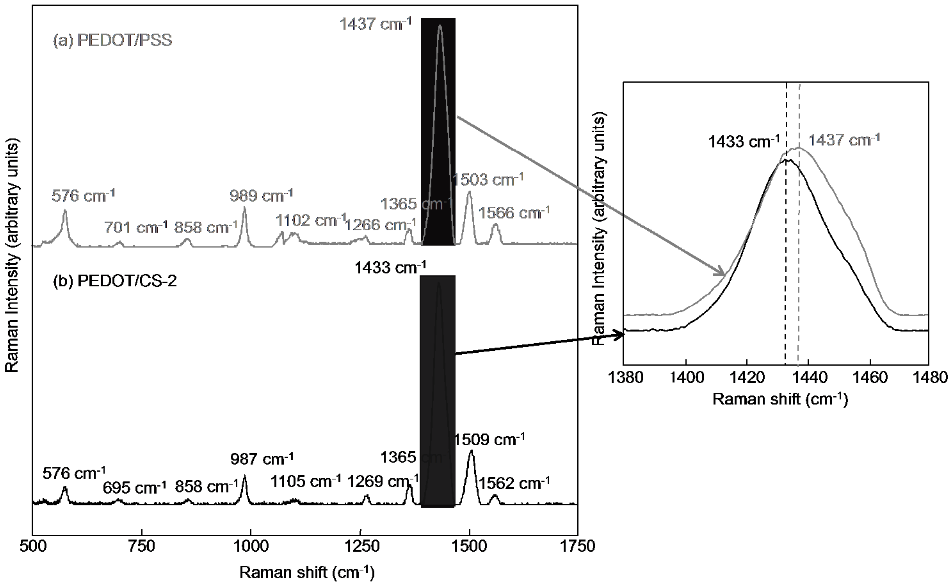


Fig. 5 Raman spectra of PEDOT/PSS and PEDOT/CS-2 films.
(a) PEDOT/PSS, (b) PEDOT/CS-2

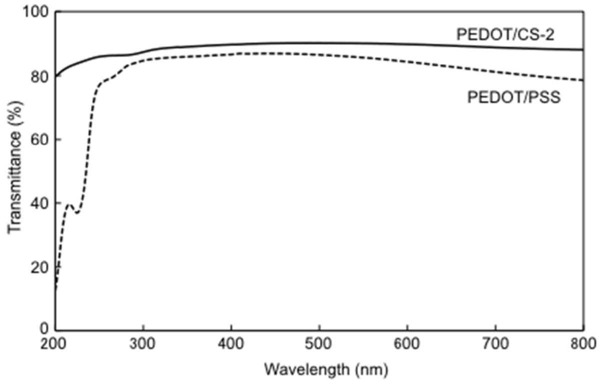


Fig. 6 Transmittance of PEDOT/PSS and PEDOT/CS-2 films.

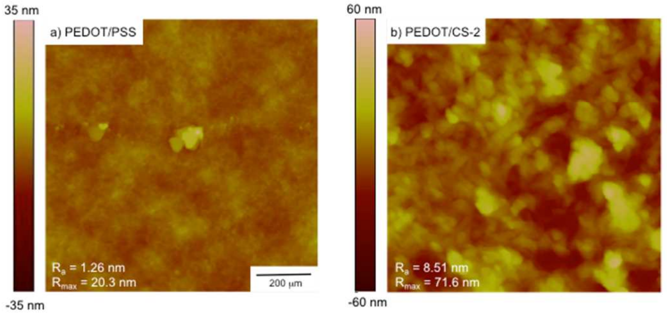


Fig. 7 AFM images of PEDOT/PSS (a) and PEDOT/CS-2 (b) films.

dependence are described in the SI. Using these films, we studied the relationship between electrical conductivity and DS, as shown in Fig. 4. As the DS of CS increased, the electrical conductivity decreased. As reported by Qin et al.[19], the sulfation in this system reveals a regioselective preference for C6 > C2 > C3, and the CS with high DS had a polymorphous structure. As shown in Fig. 2, CS-5 had a polymorphous structure and little crystalline cellulose. If more than two sulfate groups existed in a glucopyranose unit, the arrangement of EDOT in oxidative polymerization using polyanion would be disturbed. Therefore, the PEDOT molecules are most difficult to line up around CS-5. In contrast, CS-4 retains the partial crystallinity of the rigid cellulose chain. Thus, the conductivity of PEDOT/CS-4 was much higher than that of PEDOT/CS-5. The electrical conductivity of the PEDOT thin film fabricated using CS with DS = 1.03 (CS-2) was the highest of all the PEDOT/CS thin films. Its electrical conductivity was 38 times greater than that of the PEDOT/PSS film, as shown in Table 4. To investigate these phenomena, we analyzed the Raman spectra of the films.[20] Figure 5 shows the Raman spectra of the PEDOT/PSS film and the PEDOT/CS-2 films. The absorption at 1509 cm^{-1}, 1503 cm^{-1} corresponds to C_α=C_β asymmetric stretching. The strong band at 1400 - 1470 cm^{-1} corresponds to C_α=C_β asymmetric stretching. The absorption at 1365 cm^{-1} corresponds to C_β-C_β stretching, and the absorption at 1269 cm^{-1}, 1266 cm-1corresponds to C_α-C_α inter-ring asymmetric stretching. The absorption peaks at 1105 cm^{-1}, 1102 cm^{-1} and 695 cm^{-1} and 701 cm^{-1} correspond to C-O-C and C-S-C deformations, respectively. The absorption peaks at 987 cm^{-1}, 989cm^{-1} and 576 cm^{-1} correspond to oxyethylene ring deformation.[21] Figure 5 confirms the shifts in peak position and the changes in shape of both absorptions, attributed to asymmetric and C_α=C_β symmetric stretching vibrations, in the PEDOT/CS samples compared with those of the PEDOT/PSS film. The positions of the asymmetric stretching vibrations of the PEDOT/CS shifted from 1566 to 1562 cm^{-1}, and the positions of the symmetric stretching vibrations shifted from 1437 to 1433 cm^{-1}. The absorption bands of the PEDOT/CS were narrower than those of the PEDOT/PSS. As reported by

Ouyang et al., these results indicate that the PEDOT chain had a high proportion of the quinoid structure.[13]

Figure 6 shows the transparencies of the PEDOT thin films. The thickness of the PEDOT films was 50 - 80 nm. The PEDOT/PSS film exhibited absorption at 200 - 300 nm, attributable to the phenyl group of PSS. However, the PEDOT/CS films were more transparent than the PEDOT/PSS film, even at 200 - 300 nm, because CS had no functional group that adsorbed light. Using SPM, we studied the surface morphology of the PEDOT/PSS and PEDOT/CS-2 film, as shown in Fig. 7. The surface morphology of the PEDOT/PSS film was more smooth than that of the PEDOT/CS films. The surface morphology of PEDOT/CS-2 exhibited significant convexoconcavities. The PEDOT/CS-1, -3, -4, and -5 film had a morphology similar to the PEDOT/CS-2 film. As shown in Fig. 7 (a) and (b), the surface roughness (R_a) and maximum vertical interval (R_{max}) of the PEDOT/PSS film were 1.26 and 20.3 nm, respectively. In contrast, the R_a and R_{max} of the PEDOT/CS-2 film were 8.51 and 71.6 nm, respectively. Although the surface of PEDOT/CS-2 was much more irregular than that of PEDOT/PSS, the electrical conductivity of PEDOT/CS-2 was 38 times higher than that of PEDOT/PSS. Figure 8 shows X-ray diffraction patterns of PEDOT/CS-1, -2, -3, -4 -5 and PEDOT/PSS. Characteristic peaks of both PEDOT and cellulose were observed in the X-ray diffraction patterns of PEDOT/CS-1, -2, -3, -4 -5 and PEDOT/PSS (Figure S3). The peak at $2\theta = 26^\circ$ corresponded to the (200) plane of the PEDOT molecules. The peaks at $2\theta = 15.2^\circ$, 17.1°, 22.9°, and 34.7° corresponded to the (110), (101), (200), and (300) planes of crystalline cellulose, respectively. Especially, it was confirmed that the conformation of the cellulose in CS-1 and -2 almost retained the characteristic rigid structure of the cellulose chains, despite having formed a complex with PEDOT molecules in H_2O. This suggests that the PEDOT molecules lined up around the cellulose rigid chains with linear β(1→4)-linked glucopyranose residues. Figure 9 shows the relationship between the electrical conductivity of the PEDOT/CS series and the cellulose crystallinity, determined from the height of the (200) peak of cellulose at $2\theta = 22.66^\circ$. The electrical conductivity of PEDOT/CS tended to increase with the crystallinity of the cellulose. These results indicate that the PEDOT molecules more easily lined up against the CS with increasing cellulose crystallinity. This caused the electrical conductivity of PEDOT/CS-1 and 2 to become higher than that of the other PEDOT films. However, the electrical conductivity of PEDOT/CS-1 was slightly lower than that of PEDOT/CS-2. This result suggested that an appropriate amount of sulfate groups (DS of ca. 1.0) is necessary to fabricate PEDOT/CS having high electrical conductivity.

Conclusions

Using direct sulfation of cellulose, we prepared CS samples with various DS. PEDOT/CS films were prepared via in situ chemical oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) in an aqueous solution of CS, followed by spin-coating on glass substrates. We investigated the electrical conductivities of the PEDOT/CS films as a function of their DS, and found that the PEDOT film with CS (DS = 1.03) had the highest electrical conductivity, 38 times higher than that of PEDOT/PSS, despite its surface morphology exhibiting significant convexoconcavities.

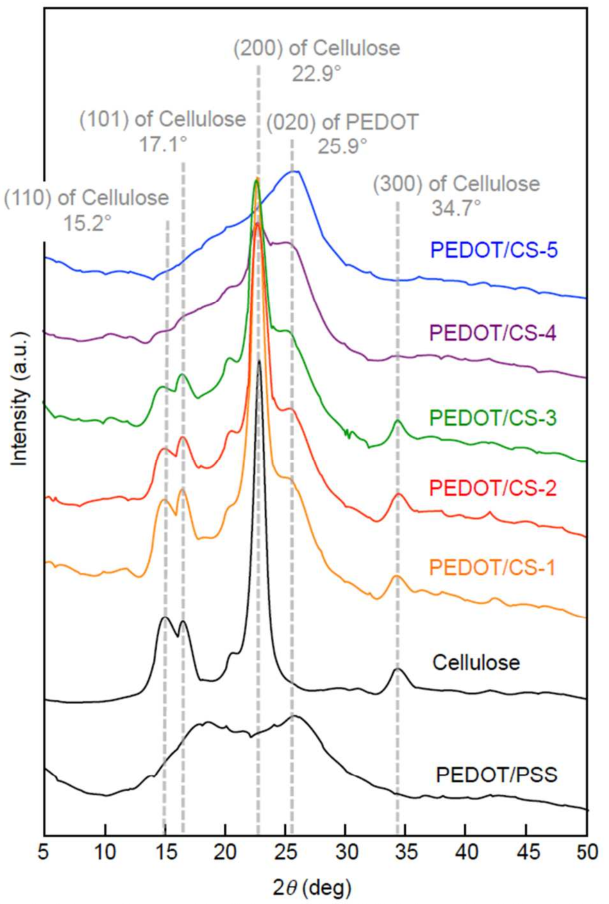


Fig. 8 XRD patterns of Cellulose, PEDOT/PSS and PEDOT/CS films.

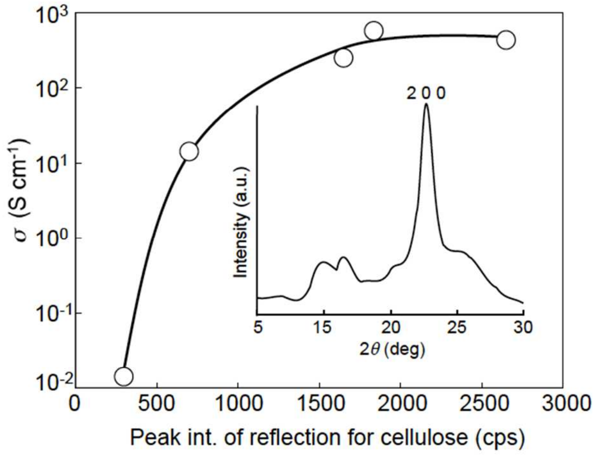


Fig. 9 Peak intensity of 2 0 0 reflection for cellulose dependence of electrical conductivity of PEDOT/CS. Inset: XRD pattern of PEDOT/CS.

Using Raman spectroscopy, we studied the conformation of PEDOT chains in the PEDOT/CS and PEDOT/PSS films. Compared with the PEDOT/PSS film, the characteristic band of the PEDOT/CS film narrowed and red-shifted from 1437 to 1433 cm^{-1}. We attributed the increased electrical conductivity of the PEDOT/CS film to an increase in the proportion of quinoid structure in the PEDOT.

The electrical conductivity of PEDOT/CS tended to increase with the crystallinity of the cellulose. The PEDOT molecules can line up around the rigid cellulose chains and easily crystallize. A reason for this is that the sulfate group of a cellulose derivative with DS: ~1.0 (CS-1, CS-2, and CS-3) can regularly arrange on the cellulose chain, in turn because this sulfate group was bonded on the 6-*O* position of the glucopyranose molecule, as reported by Zhang et al.[18] and Quin et al.[19] Thus, EDOT molecules can polymerize and form a complex, lining up around the rigid cellulose chains. It was confirmed that the electrical conductivity of PEDOT was enhanced by doping with partially crystalline sulfated cellulose. As a result, the electrical conductivity of PEDOT/CS (DS = ca. 1.0) became higher.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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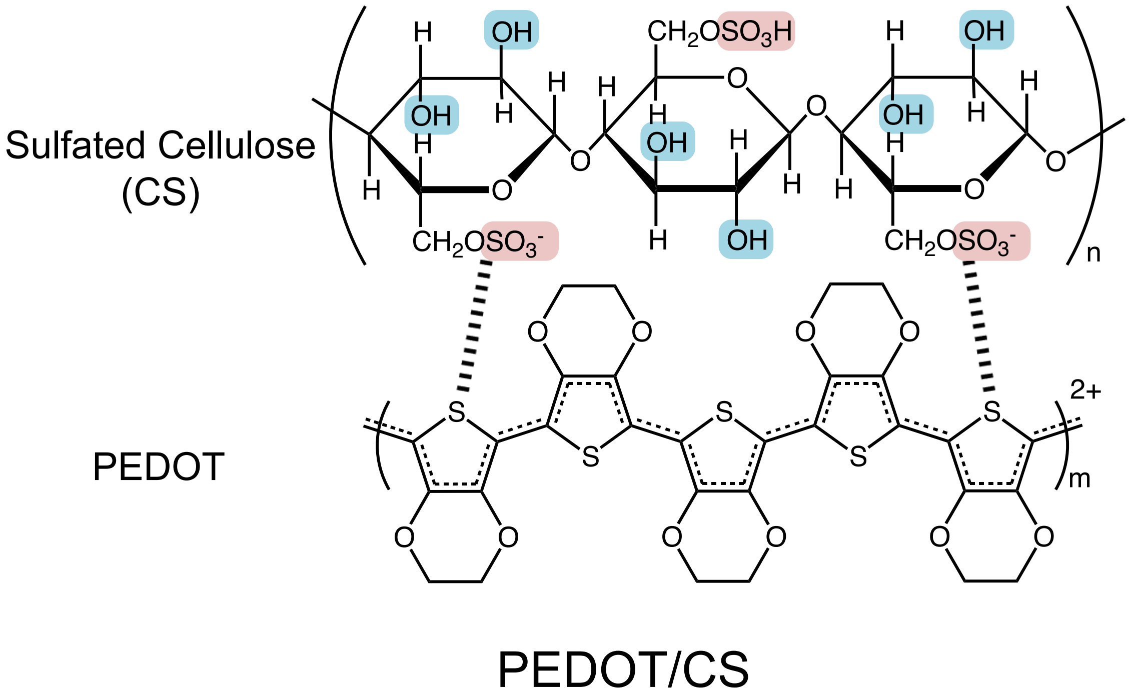

To increase the electrical conductivity of organic transparent electrodes, sulfated cellulose (CS) with a β (1→4)-linked glucopyranose chain was used as a dopant for the PEDOT system