Fabrication of Conductive Paper Coated with PEDOT – Preparation and Characterization

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Abstract

Conductive polymers have been studied extensively because of their attractive physical properties, such as conductivity, luminescent performance, and dielectric property. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most employed conductive polymers for applications, such as a buffer layer of organic electroluminescent devices, due to its high conductivity and electrical stability. In this study, we fabricated a conductive paper coated with PEDOT by direct polymerization onto a paper sheet. The conductive paper exhibited the electrical conductivity of 1.8 S/cm. Scanning electron microscopy images of the conductive paper showed two structures: thin polymer membranes attached to cellulose fibers at the surfaces, and thick polymer sheets extended through the void spaces between the fibers in the inner layers. Consequently, strong interactions between the PEDOT and the cellulose fibers enhanced mechanical properties of the conductive paper. Electron probe X-ray microanalysis (EPMA) revealed distribution elemental maps of carbon, oxygen, sulfur, chlorine, and iron on the conductive paper.

Introduction

Various paper products fulfill a myriad of daily needs in home, industrial, and laboratory settings. Conductive papers (CPs) are highly desirable electronic materials, which have received great attention.[1–4] Papers possessing electrical conductivity are expected to find

practical applications in electric instruments where they prevent a buildup of static electrical charges and in clean rooms where they fight dust accumulation. Several applications of CPs as environmentally friendly electronic materials in electromagnetic shields or as flexible electrodes are anticipated.[5–7]

A wide variety of preparation methods of CPs have been reported in recent years.[8–10] Their common issues are sensitivity of optimization and complicated procedures to fabricate CPs. Besides, most CPs exhibit their useful functions only under limited conditions.[11] As a means to add electrical conductivity to a normal paper, conductive polymer coatings have been employed.[12, 13] This approach should be convenient, simple, and inexpensive for practical applications. Polypyrroles and polyanilines have been examined as coating materials for CPs.[11, 14, 15] However, the conductivity and simplicity of the fabrication processes for these CPs still require much improvement.

We report here a new technique for the fabrication of a conductive paper composite using poly(3,4-ethylenedioxythiophene) (PEDOT, Fig. 1) as a coating material. It is well known that PEDOT has high thermostability and light resistance.[16, 17] Conductivity of PEDOT is especially high among known conductive polymers.[18] Therefore, PEDOTs are widely used for applications such as antistatic agents,[19] transparent electrodes,[20, 21] organic light-emitting displays,[22] and photovoltaic cells.[23, 24] Although many applications of PEDOT have been reported, there have been few investigations about conductive papers made using PEDOT.[25, 26] We report here the preparation of the PEDOT-coated paper (PEDOT-CP). This method provides a simple preparation process suitable for practical use.

Experimental Section

Coating

A filter paper (membrane paper) was employed as a substrate. Scanning electron microscopic images of the surface of the filter paper before coating (uncoated paper) are shown in Figs. 2a, 2c, and 2e.

Figure 3a shows an illustration of fabrication procedure for the preparation of the PEDOT-CP. 5 mL of Baytron oxidizing agent (ferric chloride and *p*-toluenesulfonate in methanol, Bayer) and 2 mL of EDOT were mixed, and then the mixture was spread over 100 mm^2 area of the filter paper with a glass rod. This operation required quick processing because the mixture underwent polymerization quickly.[27] The paper gradually turned from white to black in the ambient atmosphere as shown in Fig. 3b. This color change indicates progressive polymerization of EDOT on the paper with time. Thus, PEDOT-CP was prepared. PEDOT did not break away from the paper by washing in water.

Techniques

Chemical structure of PEDOT-CP was examined by FTIR absorption spectroscopy (FT/IR300, JEOL). The surface and cross-sectional images of PEDOT-CP were obtained using a scanning electron microscope (SEM, JSM-5610, JEOL), and elemental mapping was generated by electron probe X-ray microanalysis (EPMA, JXA-8100, JEOL). Dopant concentration of PEDOT-CP was evaluated by X-ray photoelectron spectroscopy (XPS, JPS-9010TR, JEOL). Furthermore, the mechanical properties of the PEDOT-CP were investigated by tensile testing (AUTOGRAPH-I, SHIMADZU). The electrical conductivity of the PEDOT-CP was measured by the four-probe method (MCP-T610, Mitsubishi Chemical Analytech).

Results and Discussion

IR spectra

The IR absorption spectra of the PEDOT-CP and the uncoated paper are shown in Fig. 4. These IR spectra were obtained by the KBr method. In the spectrum of the PEDOT-CP, characteristic bands at 1530–1470 and 1200–1140 cm^{-1} are observed, while the uncoated paper shows no signals in these regions. These two bands correspond to vibrations of a thiophene unit and vibrations of ether oxygen, respectively. The IR results demonstrated that the polymerization of EDOT and the coating of PEDOT onto the cellulose fibers of the filter paper were carried out successfully. Other absorption bands are very similar to those of the uncoated paper, indicating the absence of decomposition of cellulose due to the polymerization.

Scanning Electron Microscopy

The SEM images reveal visual differences between the uncoated filter paper and the PEDOT-CP as shown in Fig. 2. Spaces between paper fibrils of PEDOT-CP become narrower as shown in Figs. 2b and 2d, than that of an uncoated paper (Figs. 2a, 2c). Therefore, it can be concluded that a thin polymer layer is wrapped around the paper fibers (Fig. 5). The color of the conductive paper and the fibers is black, and no uncoated fibers appeared in the SEM images. Besides, the PEDOTs coated onto the paper show another feature in the inside cross section of the paper. A thick platelike lamellar structure appears as shown in Fig. 2b, which is absent in the uncoated paper.

The PEDOT layer present on the filter paper cannot be mechanically peeled off by rubbing, suggesting a strong adhesion of PEDOT to the paper fibers. While fine cellulose fibrils are found in the uncoated papers as shown in Fig. 2a, no fine cellulose fibrils appear in the PEDOT-CP. This suggests that a thick PEDOT layer well was coated on the fine fibrils

during the polymerization. We also examined cutting edges of an uncoated paper (Fig. 2e) and those of the PEDOT-CP (Fig. 2f). The edge part (black color) of the PEDOT-CP suggests an occurrence of penetration of the PEDOT into the cellulose fibrils.

Surface analysis

XPS measurement was conducted to evaluate the concentrations of various elements in the PEDOT-CP (Fig. 6). The specific signals of carbon, oxygen, sulfur, and iron were observed as expected (Figs. 6b–6e). Atomic percentages of these elements calculated by XPS analysis revealed that an iron atom existed per two EDOT units of PEDOT chain on the paper. The elemental mappings of these components are also shown in Fig. 7. The EPMA measurements indicated that the constituent elements had their respective distributions on the PEDOT-CP. As for carbon and oxygen, strong signals appeared from the fibers at the uppermost surfaces (Figs. 7a, 7b). Since cellulose itself is mainly composed of carbon and oxygen, this result is, therefore, plausible. On the other hand, strong signals of sulfur and iron are detected from the cross section of the PEDOT-CP (Figs. 7c, 7e). This difference in elemental distributions must be related to the two polymer textures as shown in Figs. 2b and 2d. Based on these investigations, we concluded that these two polymer textures are essentially different, and that each structure has a respective elemental component. In other words, thick plane structures of PEDOT at the deeper layers contain more sulfur and iron than those of thin PEDOT membrane structures formed around fibers of the paper surface. These observed sulfur and iron profiles are attributed to ferric *p*-toluenesulfonate that was used as a polymerization initiator. The agent also functions as a dopant to the polymer, and the resulting polarons and bipolarons as charge carriers are generated along the main chain of the polymer (Fig. 1). During polymerization, the initiator is located on the surface of the cellulose during polymerization as a catalyst. As the polymerization proceeds, the initiator is trapped inside the cellulose fibers, whereas the EDOT monomer does not reach the inside area of the fiber (Fig. 5). Thus, the unreacted portion of initiator further soaks towards the inside direction of the fiber.

Electrical conductivity and tensile strength

Visual appearance of the paper did not change appreciably with time. The paper remained black in color. In this condition, electrical conductivity of the PEDOT-CP was examined employing the four-probe method, which displayed the conductivity up to 1.8 S/cm (normal papers: $<<10^{-10}$ S/m). This value is moderate, but sufficiently high for practical applications, such as electrodes and radio-shielding materials with good processability.

In general, polymer coatings on papers cause changes in mechanical properties. To establish the mechanical effects of the PEDOT coating on the paper, tensile strength testing was carried out both for the uncoated paper and the PEDOT-CP. As shown in Table 1, the

value of breaking load increased dramatically up to ca. 34 times upon coating, suggesting that the PEDOT coating improves tensile strength. The interlocking between the cellulose fibers and PEDOT strengthens the tensile property. On the other hand, a degree of breaking elongation decreases from 7.0% to 1.1%. A large number of fine fibrils extended from the main fibers of the uncoated papers (as seen in Fig. 2c) resulted in the high elongation property of the original paper. The PEDOT layer fixes and covers the fibrils tightly as shown in Fig. 8, resulting in high rigidity and a decrease of elasticity.

Conclusions

A conductive paper was fabricated by the EDOT monomer painting / simultaneous polymerization method for the formation of PEDOT / cellulose composite. The PEDOT-coated conductive paper has good processability characteristics, such as normal papers. The SEM observation revealed that a thin PEDOT layer covers the cellulose fibers. The electrical conductivity of the PEDOT-coated paper was estimated to be 1.8 S/cm. This value is as high as that reported in recent studies using polypyrroles and polyanilines, and is sufficiently high for practical applications. Tensile strength of the paper was drastically increased after the PEDOT coating due to the fact that PEDOT strengthens individual cellulose fibers and produces inter-fibril connections. The conductive paper thus prepared may be a promising material for industrial applications.

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Table 1. Mechanical properties of PEDOT-CP and uncoated paper.

		Maximum load (N)	Elongation (%)	Breaking load (N)	Breaking elongation (%)
Uncoated paper	1	14.2	3.3	1.02	6.0
	2	15.1	3.5	0.99	8.1
	3	16.0	4.3	1.04	7.9
	4	14.7	3.7	1.03	6.2
	average	**15.0**	**3.7**	**1.02**	**7.0**
PEDOT-CP	1	34.6	1.0	34.6	1.0
	2	33.3	0.9	33.3	0.9
	3	35.8	1.1	35.4	1.1
	4	33.7	1.2	33.4	1.2
	average	**34.4**	**1.0**	**34.2**	**1.1**

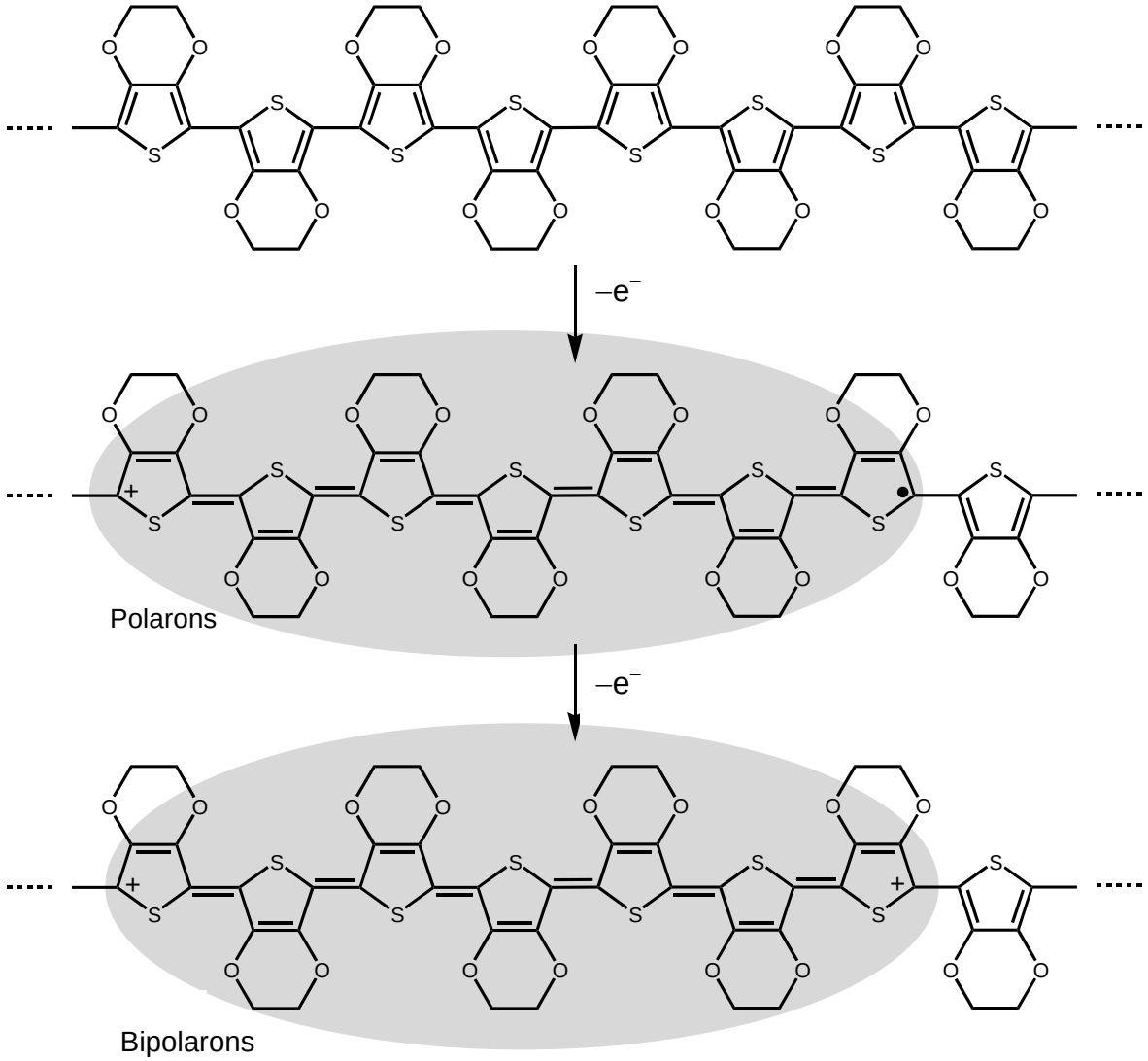

Figure 1. A chemical structure of poly(3,4-ethylenedioxythiophene) (PEDOT) and its polaron and bipolaron states.

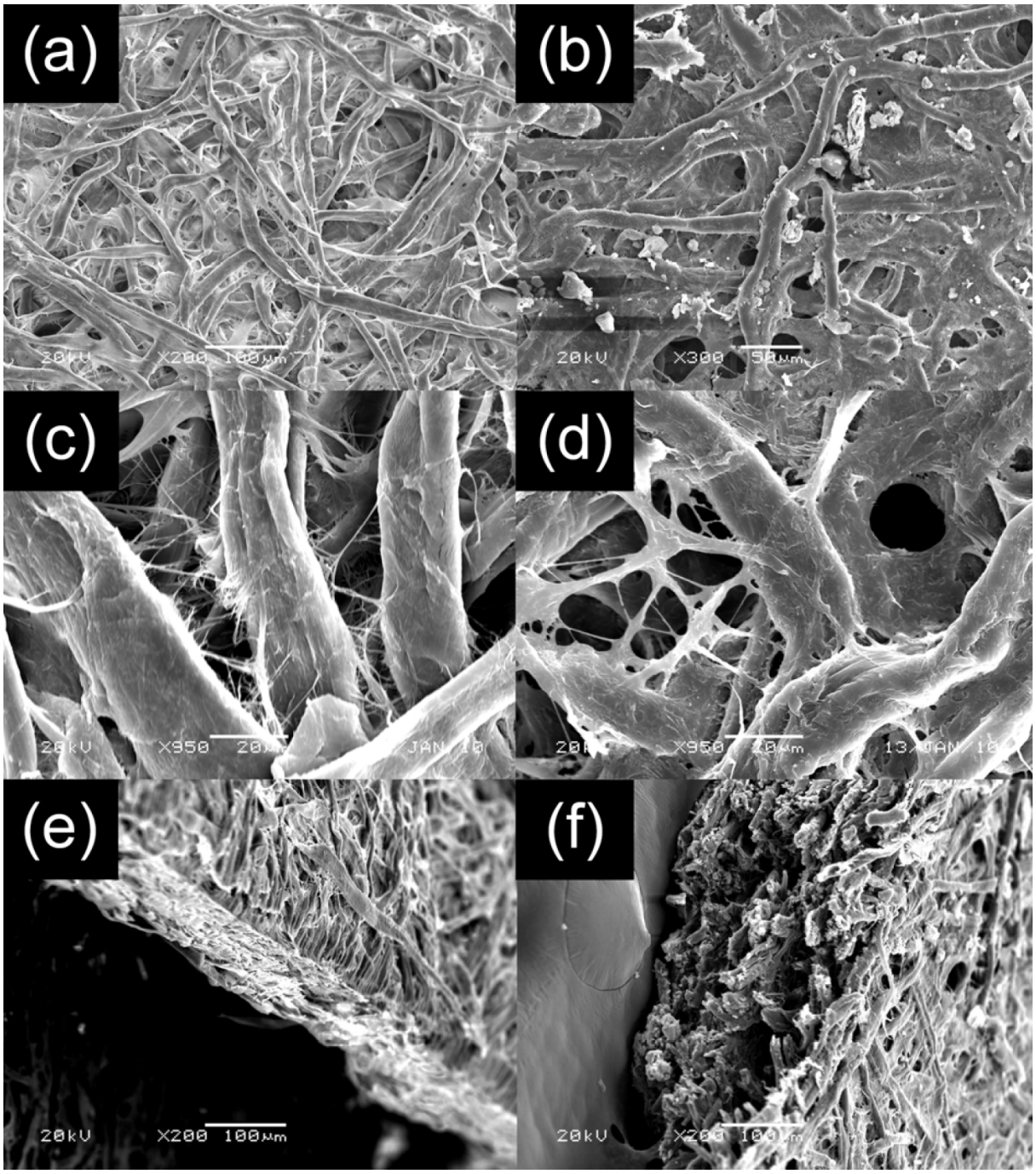

Figure 2. SEM images of uncoated paper (a, c, e) and PEDOT-CP (b, d, f).

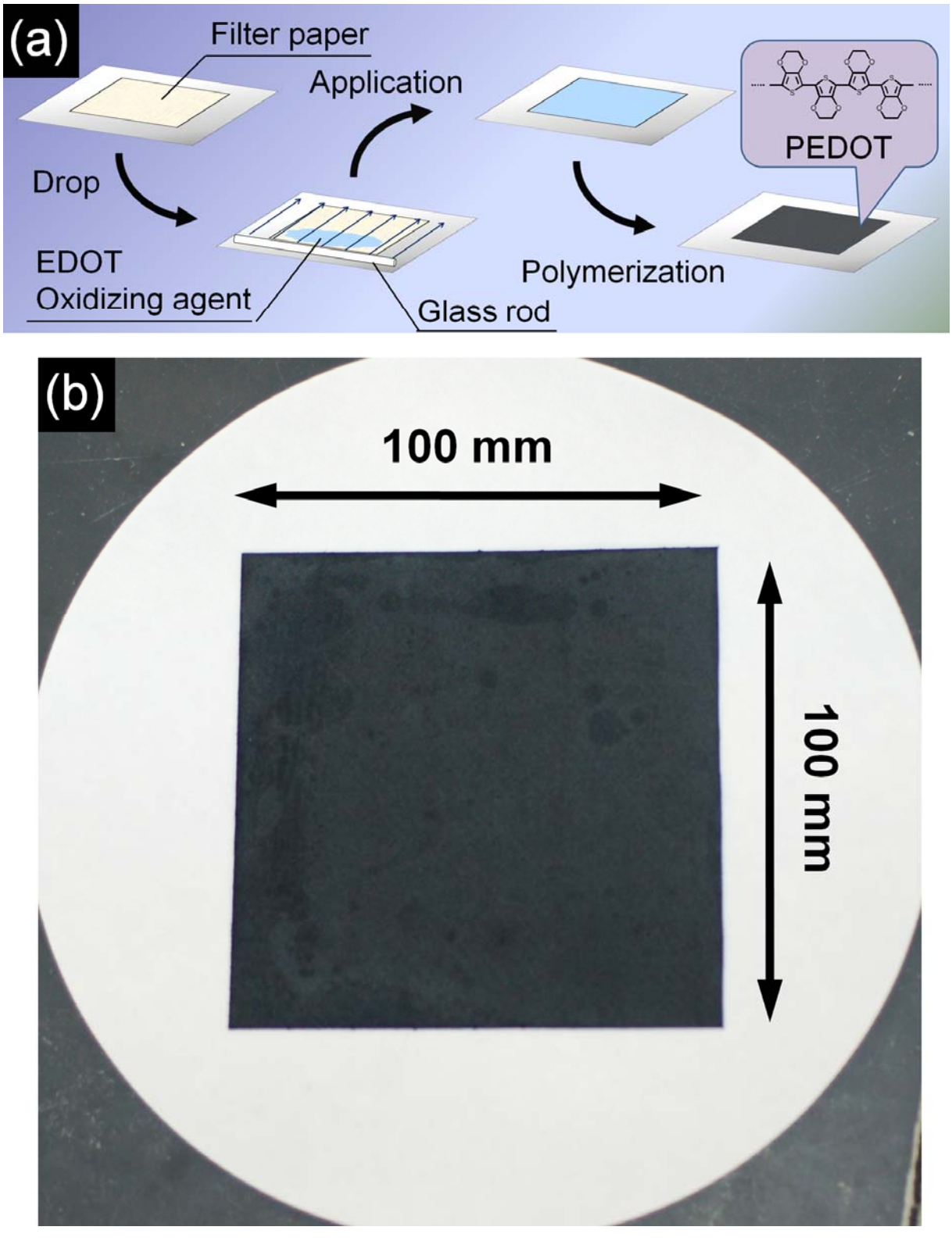

Figure 3. (a) In situ polymerization methods for fabrication of PEDOT-CP. (b) An overview of PEDOT-CP.

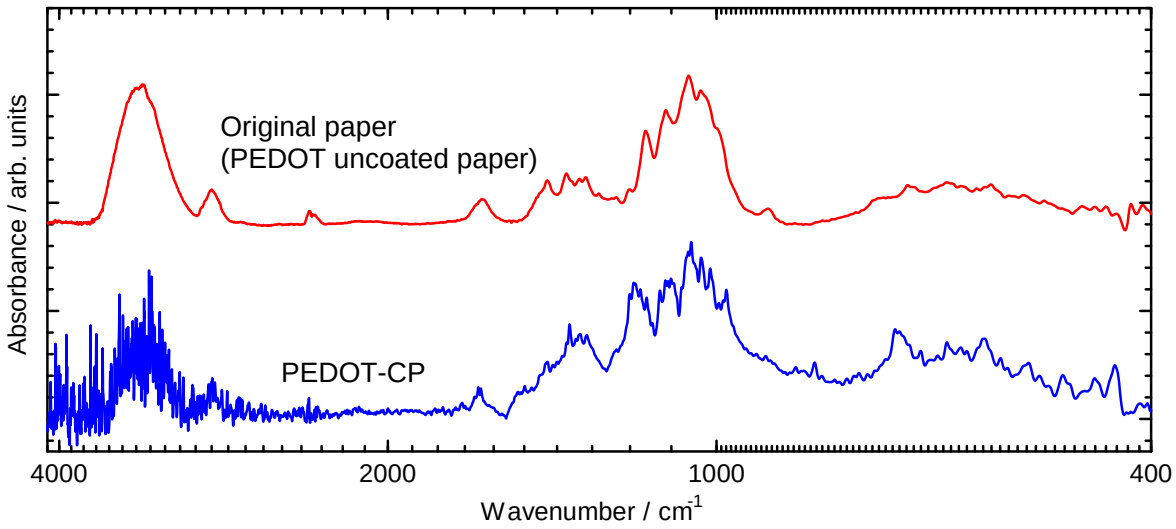

Figure 4. IR spectra of original paper and the conducting paper coated with PEDOT (PEDOT-CP).

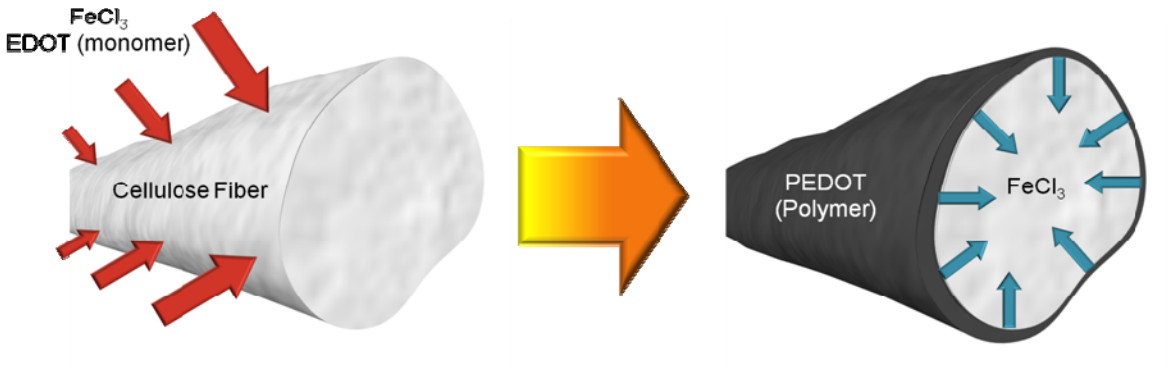

Figure 5. Illustration of PEDOT coating on the cellulose fibrils.

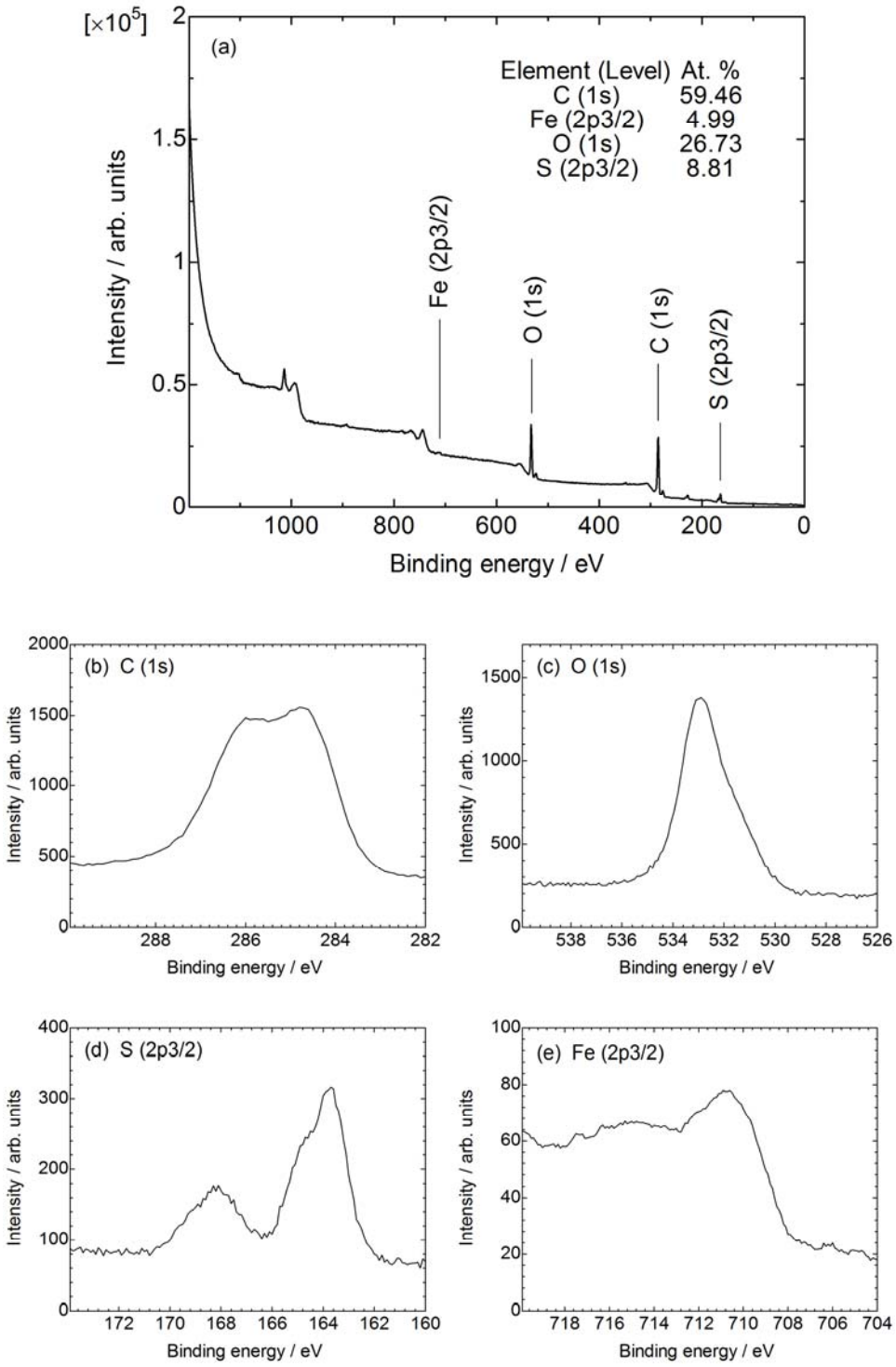

Figure 6. (a) XPS wide scan spectrum of PEDOT-CP and (b)-(e) narrow scan spectra of C, O, S, and Fe in PEDOT-CP.

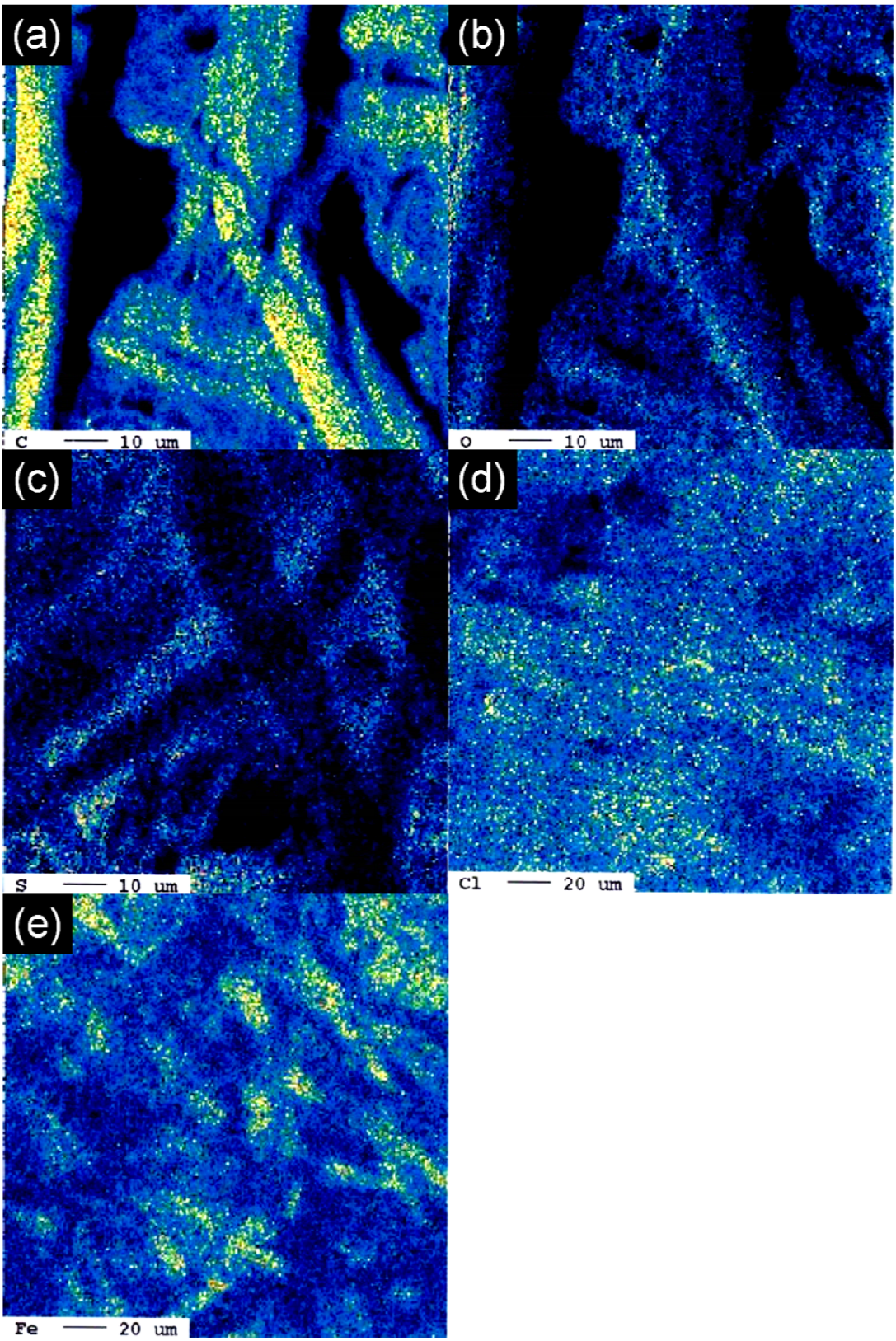

Figure 7. Two-dimensional mapping images of carbon, oxygen, sulfur, chlorine and iron obtained by EPMA.

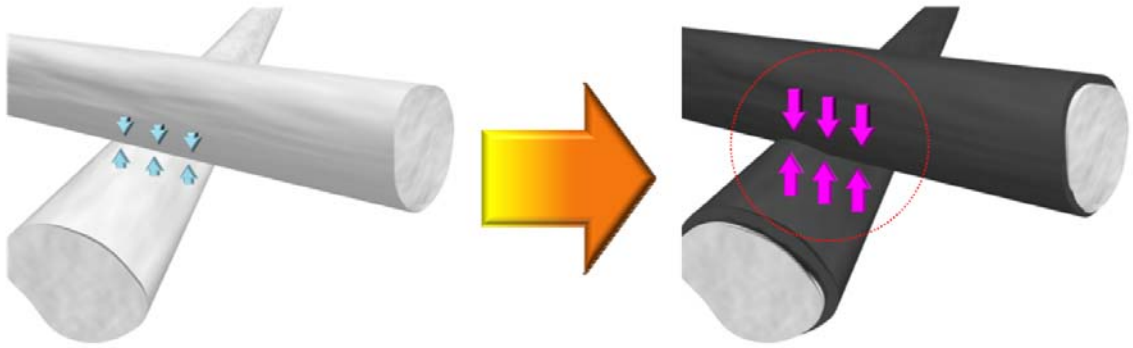

Figure 8. Interconnections between cellulose fibrils and PEDOT.