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Electrospray Deposition of PEDOT-PSS and Electrochemical Characterization

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1. Introduction

As a electroconductive polymer, poly (3, 4-ethylene dioxythiophene) - poly (styrene sulfonate) (PEDOT-PSS) is drawing attention for such applications as hole transport or injection layers of organic LEDs. PEDOT-PSS also shows electrochromism, which makes it attractive for display and recording media. So far, its thin films have been prepared by conventional wet-processes such as spin coating. This paper proposes a new film deposition technique for PEDOT-PSS by using the electrospray deposition (ESD) method.

The electrospray is a technique that atomizes liquid solution from the tip of a capillary under high electric field, and has the possibility of atomizing wide range of organic materials directly from their solution without damaging the molecules. It has been used as the ion source for mass-analyzer as well as for depositing thin films, particles and nano-fibers [1]. The microstructure of deposits is largely influenced by the spray conditions such as solution composition and spray voltage. It is expected that the ESD surpasses the conventional wet-coating processes at efficient use of source material. However, there have been few reports on ESD of conductive polymers because conductive liquids are generally difficult to electrospray. This paper reports the optimization of ESD condition for depositing smooth and uniform PEDOT-PSS films. The deposited films were characterized by electrochemical measurement.

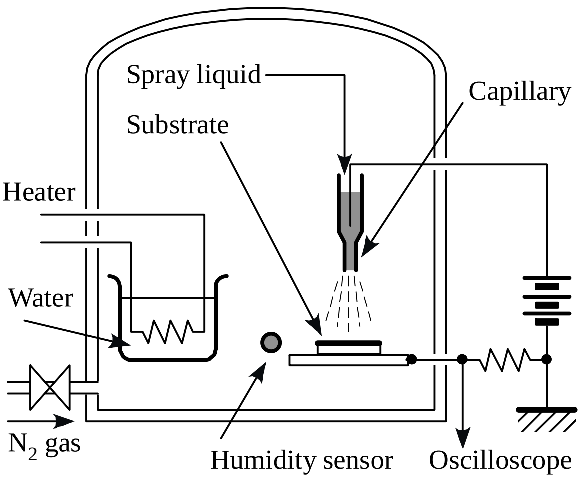

Fig. 1 Schematic diagram of ESD apparatus.

2. Experiments

Figure 1 shows the experimental setup of the ESD apparatus. PEDOT-PSS aqueous suspension was charged in a capillary, either a stainless steel (SUS) tube of 0.2 mm inner diameter or a glass capillary of 0.08 mm inner diameter, which was placed above 17 mm from the substrate surface. The electrospray was achieved at a spray voltage of 8 kV and a spray current of around 10 μA. Films of about 200 nm thick were deposited by spraying for 10 min. The deposition was performed in a steel chamber purged with nitrogen gas. The humidity was controlled by adjusting the nitrogen flow and by evaporating pure water inside the chamber. Indium-tin oxide (ITO) coated glass was used as the substrate. PEDOT- PSS suspension was commercially obtained from Aldrich as 2.8 wt% dispersion in water. In order to optimize the spray condition, the commercial suspension was diluted with pure water and buthanol.

3. Results and Discussions

Spray Liquid

The commercial PEDOT-PSS suspension did not form any spray in the above-mentioned condition, even by increasing the spray voltage to 10 kV. It is reported that lower electrical conductivity and lower surface energy are preferable for inducing electrospray. The commercial suspension was diluted with pure water to 70 wt%, but the electrospray was still impossible. On the other hand, electrospray was observed by diluting the commercial suspension with buthanol to 50 wt%. However, the spatial uniformity of the spray was poor with this condition. It was found that the optimum spray can be generated by mixing the commercial suspension, pure water and buthanol at a weight ratio of 2:2:1.

Surface Morphology

It is reported that the structure of ES deposits are largely influenced by the spray condition, and the deposits frequently assume the forms of particles and fibers [1]. Scanning electron microscopy revealed that the ESD films of PEDOT-PSS tend to have granular structure, suggesting that the electrospray generates small droplets of PEDOT-PSS suspension rather than atomizing the polymer molecules. As a consequence, the film structure is dependent on the process how the droplets dry into solid state. Figure 2 shows the surface morphology of the films deposited with SUS (a-c) and glass (d-e) capillaries in different humidity conditions. In the present case, the SUS capillary appeared to generate larger droplets compared to the glass capillary. As a consequence, the film deposited with glass capillary had granular structure presumably because the droplets sprayed from the glass capillary can dry before reaching the substrate to form a film by coagulation of solid particles. On the other hand, the film deposited with SUS capillary have larger portion of flat surface because larger droplets can reach the substrate surface in liquid state, where they form flat meniscus and dry into planar solid film afterwards. Accordingly, the film morphology is strongly influenced by the environmental humidity that governs the evaporation of solvent. It was found that flat and uniform thin films can be obtained with both capillaries when the humidity in the deposition chamber was increased to 80%.

Electrochemical Characteristics

Electrochemical property of the film was measured in 0.1 M propylene carbonate solution of $LiClO_4$. Figure 3 shows cyclic voltammogram of the PEDOT-PSS films deposited by spin-coating and by ESD with SUS and glass capillaries in humidity of 40%. Reversible reduction was observed at -1.4 V (vs Ag/Ag^+) for the ESD film by SUS capillary as well as the spin-coated film. On the other hand, the ESD film by glass capillary, which had nonuniform granular structure as shown in Fig. 2 (e), did not show clear redox peaks. This result points out the importance of controlling the film morphology in the process of film formation.

Accompanying to the reduction, electrochromic color change was observed from almost transparent to dark blue. Change of the optical transmission spectra was measured for an electrochromic cell that was prepared by pressing the $LiClO_4$ electrolyte liquid layer in between two ITO substrates, one of which baring the PEDOT-PSS film. Figure 4 shows the transmission spectra observed at reduced and oxidized states at the cell voltages of -4 and 1.5 V, respectively. Although the reduction is not complete at this point due to the insufficient amount of electrolyte in the cell, this preliminary result indicates that the ESD films of PEDOT-PSS have potential application for optical and optoelectronic devices.

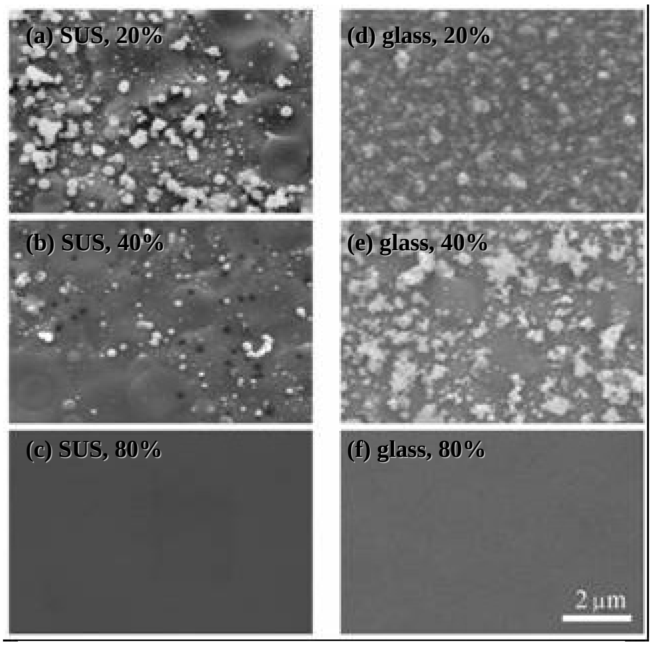

Fig. 2 Surface morphology of PEDOT-PSS films deposited with SUS (left) and glass (right) capillaries at humidity of 20, 40 and 80% (top to bottom).

3. Conclusions

Electrospray deposition of smooth PEDOT-PSS thin films was made possible by optimizing the composition of spray liquid and humidity of deposition space. Surface smoothness was improved by adjusting the humidity during film formation, which was effective in enhancing electrochemical functionality. In conclusion, ESD is expected to have potential applicability as a unique film deposition technique for functional organic materials.

References

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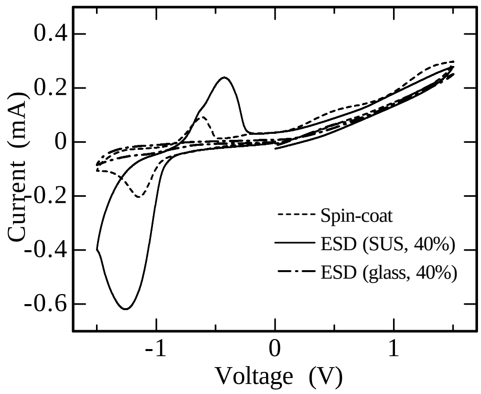

Fig. 3 Cyclic voltammogram of PEDOT-PSS films deposited by spin coating and by ESD with SUS and glass capillaries at humidity of 40%.

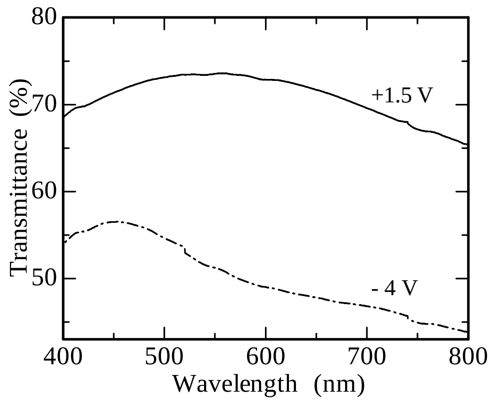

Fig. 4 Optical absorption spectra showing electro-chromism of PEDOT-PSS film deposited with SUS capillary at humidity of 40%.