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SHORT COMMUNICATION

Highly Conductive and Transparent Poly(3,4-ethylenedioxythiophene)/Poly(4-styrenesulfonate) (PEDOT/PSS) Thin Films

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We have investigated centrifuge effect on the poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (denote PEDOT/PSS) films prepared by a spin-coating coupled with a solvent-treatment, by a dynamic light scattering, a scanning transmission electron microscopic, an atomic force microscopic, and ultraviolet-visible spectroscopic measurements, in terms of electrical conductivity and optical transmittance. As a result, we have successfully prepared highly conductive (443 S/cm) and transparent (89%) PEDOT/PSS thin films with thickness of 93 nm by the combination of three approaches, *i.e.*, centrifuge, spin-coating and solvent-treatment.

KEY WORDS: Conductive Polymer / PEDOT/PSS / Thin Film / Transparent Electrode / Colloidal Dispersion /

Since the "solubility" was realized by using a water-soluble polyelectrolyte poly(4-styrenesulfonate) (PSS),[1] poly(3,4-ethylenedioxythiophene)/poly(4-styrene sulfonate) (PEDOT/PSS) has been extensively studied from viewpoints of academic and technologic aspects.[2–5] The PEDOT/PSS has been a widely available conductive polymer since the colloidal dispersion of the PEDOT/PSS in water could easily provide films on various substrates by simple means such as solution casting and spin-coating techniques.

Recently we have reported correlation between sizes of colloidal particles and minimum thickness of spin-coated thin films of PEDOT/PSS studied by a dynamic light scattering (DLS), a scanning transmission electron microscopy coupled with an energy dispersive X-ray spectroscopy (STEM-EDX), C_{60}-sputtering X-ray photoelectron spectroscopy (XPS), and an atomic force microscopy (AFM).[6] As a result, PEDOT/PSS thin films spin-coated at 3000 rpm, are suggested to be primary nanoparticle-"monolayer"s, based on the results of STEM-EDX, DLS, and XPS measurements. The AFM and conductive-probe microscopic images revealed that the PEDOT/PSS primary nanoparticles do not packed compactly within the thin films. Such thin films showed high transparency but poor conductivity.

Principally PSS-layer-removed PEDOT/PSS nanoparticles with narrow size distributions would result in compactly packed nanoparticle-thin films which can be expected to show both high conductivity and transparency.

Herein we present significant enhancement on electrical conductivity of spin-coated PEDOT-PSS thin films by centrifuge and solvent effects, while high transparency maintained. The PEDOT/PSS thin film with 93-nm thickness showed electrical conductivity of 443 S/cm and visible light-transmittance of 89%.

EXPERIMENTAL

20 mL of PEDOT/PSS (BAYTRON PH500) solution was separated by a centrifuge at 4000–5000 rpm and the upper layer of the solution was decanted. The upper layered solution was freeze-dried to obtain PEDOT/PSS powder. The powder was re-dispersed in deionized water under ultrasonication, resulting in PEDOT/PSS solution with a concentration of 2 wt %. 9 mL of the 2 wt % solution with or without ethyleneglycol (EG) was dropped on the silicon wafer. The spin-coatings were performed at rotation speed of 3000 rpm for 1 min at atmospheric circumstance. After the spin-coating the samples on the silicon wafers were dried at 160 °C for 1 h in a vacuum oven.

The PEDOT/PSS films protected by platinum and carbon depositions and sliced by a focused ion beam (FIB) into thin piece of cross-section, were used for the STEM observations. AFM measurements were carried out with a scanning probe microscope (SPM-9600, Shimadzu) by a tapping mode. For the AFM measurements the PEDOT/PSS thin films on the SiO_2/silicon wafer (5×5 mm) were used. Transmittance at wavelength of 300–800 nm were measured by UV-vis spectrometer (V-670, Jasco) using the PEDOT/PSS films prepared by the spin-coating on quartz substrates instead of the silicon ones. Electrical conductivity was measured by a four-probe technique (Loresta-GP MCP-T610).

RESULTS AND DISCUSSION

The PEDOT/PSS films prepared from 2 w% re-dispersed solution of the freeze-dried PEDOT/PSS powder after centrifuge at 5000 rpm, with or without EG 3%, were observed by the STEM, as shown in Figure 1.

Thicknesses of the films both without (A) and with (B) EG 3% were measured to be 93 nm. The value is much larger than that of the film prepared from pristine solution, 16 nm which is previously observed by us.[6] Concentration of the re-dispersed solution, 2 w% is higher than that of the pristine one, 1.6 w%. The higher concentration is considerable to result in aggregate-packed film with a larger thickness. Such thick film only showed lower conductivity of less than 0.4 S/cm if prepared without EG. Addition of 3% EG enhanced the conductivity to 87 S/cm. The addition of EG, however, did not influence the film thickness, as shown in Figure 1. Furthermore, it is easily considered that the film prepared from the pristine powder or the powder with centrifuge-treated at less than 5000 rpm should have the similar or larger thickness. Therefore we can estimate the conductivity of the films by using the thickness value of 93 nm.

The centrifuge effect on conductivity and surface roughness were investigated in detail. Figure 2 shows rotation speed-dependent conductivity (A) and surface roughness (B). The electrical conductivity significantly increased with increasing in the rotating speed of centrifuge. It is considerable that the PEDOT/PSS colloidal particles with a narrower size distribution more compactly pack each other in the thin film, resulting in

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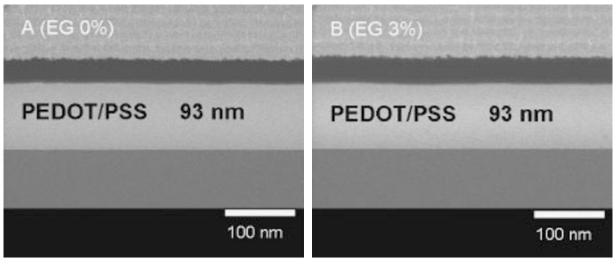

Figure 1. STEM images of the PEDOT/PSS thin films spin-coated from PEDOT/PSS dispersion without EG (A) and with 3% EG, respectively.

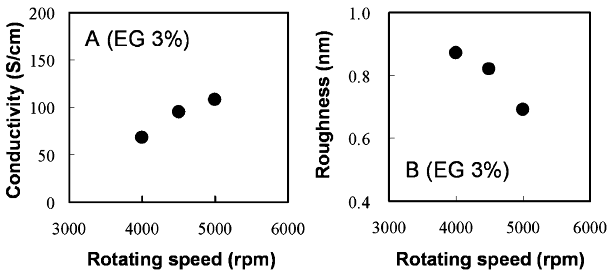

Figure 2. Plots of electrical conductivity (A) and surface roughness (B) of the PEDOT/PSS thin films against rotating speed of centrifuge.

higher conductivity. On the other hand, the surface roughness decreased with increasing in the rotating speed. It is also indicative that the size distribution of the packed PEDOT/PSS particles is narrower, resulting in more smooth surface of the thin film. It is noted that the increasing trend of the conductivity induced by the centrifuge effect cannot be changed qualitatively even though the estimated thickness was used for the calculation of the conductivity.

Previously we have optimized the solvent effect of EG on the conductivity of thick PEDOT/PSS films with several µm-thickness, indicating that 3% is the best concentration for the pristine PEDOT/PSS dispersion. In previous study we also confirmed that the addition of EG made PSS:PEDOT molar ratio decreased, based on XPS measurement, which was reported elsewhere[7] (also see Supporting Information (SI)). The PEDOT/PSS concentration (2%) of the dispersion in the present study, however, is higher than that (1.6%) of the pristine dispersion. Therefore, we have carefully re-optimized the EG concentration in terms of conductivity and transmittance of visible-light, as shown in Figure 3. The conductivity increased with increasing in the EG concentration while the transmittance was unchanged. The highest estimated value of the conductivity, 443 S/cm was obtained at the EG concentration of 7%, coupled with high value of the transmittance of 89% (also see SI). The surface roughness also was not changed by the addition of EG (see SI). One of the proposed mechanism of the conductivity enhancement is that excess PPS molecules are washed away from the particle or film surface with replacement of the EG, while the PSS anions functioned as the dopants still remain in the particle or film.[8] It should be noted that the film prepared under the same condition but only without the centrifuge showed only moderately high conductivity, 263 S/cm, which clearly reveals the enhancement of conductivity by the

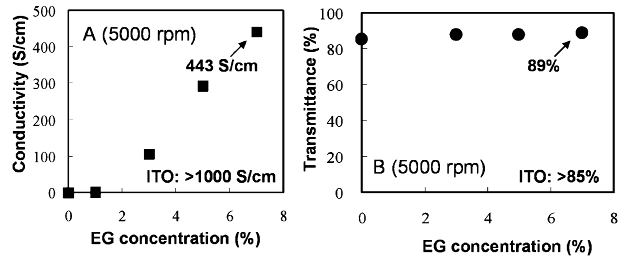

Figure 3. Plots of electrical conductivity (A) and visible-light transmittance (B) of the PEDOT/PSS thin films against concentration of EG in the PEDOT/PSS dispersion used for the spin-coating.

centrifuge which would result in narrower size distribution of the PEDOT/PSS colloidal particles.

In conclusion we have successfully prepared highly conductive (443 S/cm) and transparent (89%) PEDOT/PSS thin films with thickness of 93 nm by the combination of three approaches, *i.e.*, centrifuge, spin-coating and solvent-treatment. The thin films potentially could replace indium-tin-oxide (ITO) electrode currently used in touch screens. A possible mechanism for the enhancement of the conductivity is that narrower particle size distribution by the centrifuge, and elimination of PSS surface layer of the PEDOT/PSS particle by the EG enhance the conductivity (see SI). The detailed study for the mechanism is underway.

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Electronic Supporting Information Available: Figures S1–S4. These materials are available *via.* the Internet at http://www.spsj.or.jp/c5/pj/pj.htm

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