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Synthesis of highly conductive PEDOT:PSS and correlation with hierarchical structure

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ABSTRACT

The water dispersions of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonic acid) (PEDOT:PSS) as colloidal particles were synthesized by oxidative polymerization with different composition ratios of repeating units for PSS and PEDOT ($\alpha = 1.4–8.3$). The role and effect of the PSS on hierarchical structure and electrical conductivity of the PEDOT:PSS were investigated systematically by means of X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), zeta potential, X-ray diffraction (XRD), and conductive atomic force microscopy (c-AFM). It was found that the PEDOT:PSS colloidal particles stably dispersed in water at $\alpha \geq 2.3$, while small primary particles aggregated to form large secondary particles in water at $\alpha = 1.4$ because the zeta potential dropped owing to the less PSS. The PEDOT:PSS showed paracrystalline structure where highly conductive PEDOT nanocrystals uniformly distributed in the less conductive PSS matrices. The electrical conductivity was strongly dependent on the composition ratio and attained as high as 700 S/cm at $\alpha = 2.3$ where a positive correlation was seen between the electrical conductivity and number of conductive particles favorable for hopping of charge carriers in between the nanocrystals.

1. Introduction

The organic electronics originated from low cost, lightweight, and flexible electronics is developing through printed electronics, stretchable electronics, and recently into wearable electronics for Internet of Things (IoT) applications such as flexible displays, smart sensors, and soft actuators. Here, wet-processable, flexible, and highly conductive polymers are of great advantages to the organic electronics. Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate acid) (PEDOT:PSS), commercially available in the form of water dispersion as colloidal particles, can be applied to antistatic coatings, solid electrolytic capacitors, and organic LEDs [1–5]. Moreover, because of the high electrical conductivity, transparency, and thermal stability, the PEDOT:PSS has attracted considerable attention for transparent electrodes of flexible displays, touch panels, and solar cells as an alternative of indium tin oxide (ITO) [6]. Importantly, such excellent electrical characteristics of the PEDOT:PSS essential for the organic electronics are strongly dependent on its hierarchical structure [7–16]. Furthermore, the electrical conductivity of the PEDOT:PSS is improved significantly by two orders of magnitude upon adding high boiling point solvents such as ethylene glycol (EG) and dimethyl sulfoxide, so-called 'secondary dopant' [17–22]. The mechanism was explained in terms of changes in the hierarchical structure: Crystallization of the PEDOT molecules, removal of the insulating PSS surrounding the PEDOT core, and aggregation of the PEDOT:PSS colloidal particles, which affect both intra- and inter-particle transport of charge carriers [9,23,24].

For further improvement of the electrical conductivity, a correlation between the hierarchical structure and electrical conductivity of the PEDOT:PSS should be clarified in more detail. In particular, the secondary structure (poly-ion complex) is a key structure affecting both tertiary (colloidal gel particle) and quaternary structures (aggregation) in order to optimize the transport of charge carriers in the solid state [15]. However, a few studies on synthesis and characterization of the PEDOT:PSS reported extremely low electrical conductivities [26,27], and therefore the effect of composition ratio between the PEDOT and PSS on the hierarchical structure and high electrical conductivity of the PEDOT:PSS is still a 'black box'.

In this study, we newly synthesized highly conductive PEDOT:PSS water dispersions by oxidative polymerization with

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various feed composition ratios of PSS repeating unit to EDOT monomer ($\alpha_{feed} = 1–10$) and changes in the hierarchical structure and electrical conductivity of the PEDOT:PSS were investigated by means of X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), zeta potential, X-ray diffraction (XRD), and conductive atomic force microscopy (c-AFM). The results allowed us to conclude that the composition ratio was crucially important for the higher-ordered structure and electrical conductivity of the PEDOT:PSS, in which a number of conductive PEDOT nanocrystals uniformly distributed in the insulating PSS matrices were favorable for hopping of charge carriers and led to the highest bulk conductivity as high as 700 S/cm.

2. Experimental

2.1. Synthesis of PEDOT:PSS

The water dispersions of PEDOT:PSS colloids with various feed composition ratios (α_{feed}), defined as the molar ratio of PSS repeating unit to 3,4-ethylenedioxythiophene (EDOT) monomer, from 1 to 10 were synthesized by oxidative polymerization of EDOT (Aldrich) in the presence of various concentrations of the PSS ($M_w = 75{,}000$ g/mol, Aldrich). The EDOT (0.5 wt%) and PSS (0.2–6.5 wt%) were mixed in pure water containing 0.98 wt% of $Na_2S_2O_8$ (Junsei Chemical) as an oxidant and 0.2 wt% of $FeSO_4\,7H_2O$ (Junsei Chemical) as a catalytic agent. The total volume of reaction solution was typically 1.2 L and the oxidative polymerization was carried out under vigorous stirring in a nitrogen stream at 20 °C for 24 h. After polymerization, the resulting sodium, iron, and sulfate ions were removed by cation exchange (Lewatit Monoplus S108H, Lanxess) and anion exchange resins (Lewatit MP62WS, Lanxess). The solid films were fabricated by casting the PEDOT:PSS water dispersion (1 wt%) containing 5 wt% of ethylene glycol (EG) as a secondary dopant [9,23,24] on a glass substrate at 200 °C with a moisture analyzer (MOC-120H, Shimadzu).

2.2. Measurements

The median diameter (D_{50}) and zeta potential of the PEDOT:PSS colloidal particles were evaluated by a dynamic light scattering (DLS) method at 25 °C with particle size analyzer (Nanotrac UPA-UT151, MicrotracBEL) and zeta potential analyzer (DelsaNano C, Beckman Coulter), respectively. The actual composition ratio (α) of repeating units for PSS and PEDOT in the PEDOT:PSS thin films spin-coated on n-Si wafer was evaluated by X-ray photoelectron spectroscopy (XPS) with a XPS photometer (JPS-9200, JEOL) using monocromatized Al (K_α) X-ray with an incident angle of 10°. The X-ray diffraction (XRD) patterns were measured using an imaging plate (R-AXIS DS3C, Rigaku) at 40 kV and 30 mA with an exposure time of 1 h. The conductive atomic force microscopic (c-AFM) measurements were carried out with a scanning probe microscope (SPM-9600, Shimadzu) equipped with a conductive probe, where height and current images were measured by a contact mode under a bias voltage of 0.1 V. The electrical conductivity of the PEDOT:PSS film was measured by a normal four-point method with a Loresta-GP (MCP-T610, Mitsubishi Chemical Analytech), where thickness of the PEDOT:PSS film was evaluated with a stylus profilometer (D-100, KLA-Tencor).

3. Results and discussion

3.1. Composition ratio of poly-ion complex (secondary structure)

The secondary structure of PEDOT:PSS poly-ion complex is formed through electrostatic interactions between PEDOT cations and PSS anions where the PSS has two functions: One is the dopant to compensate positive charges of the PEDOT in the state of polaron or bipolaron. The other is the dispersant for stably dispersing hydrophobic PEDOT in water as the poly-ion complex [28]. Therefore, the composition ratio of the poly-ion complex will be one of the key parameters affecting the dispersion state of the PEDOT:PSS colloidal particles. Fig. 1 shows XPS spectra of the PEDOT:PSS in the energy range of the S 2p signal, where two peaks at binding energies of 163 and 167 eV assigned to the sulfur atoms of PEDOT and PSS, respectively [29]. It was found that relative intensity of the PSS to PEDOT increased with increasing the α_{feed}, where actual composition ratios (α) evaluated from the peak areas of the XPS spectra were in good agreement with the values of α_{feed} as shown in the inset of Fig. 1.

3.2. Median diameter and zeta potential of colloidal particles (tertiary structure)

The effect of composition ratio on median diameter (D_{50}) and zeta potential of the PEDOT:PSS colloidal particles was investigated by means of the DLS as shown in Fig. 2. At $\alpha = 2.3–8.3$, a sharp monodisperse peak was observed with the D_{50} of 17–29 nm, similarly to the commercial grades of the PEDOT:PSS (PH500 and PH1000, Heraeus) [12], where zeta potential was found to be −86–−89 mV. This indicates that a negatively charged PSS-rich layer covers on the surface of the PEDOT:PSS colloidal particles, which is responsible for the stable dispersion in water. On the other hand, at $\alpha = 1.4$, the D_{50} significantly increased to 218 nm while the zeta potential dropped, demonstrating aggregation of the PEDOT:PSS colloidal particles caused by poor dispersibility in water due to the less PSS.

3.3. Crystalline structure of PEDOT (tertiary structure)

In order to elucidate the dependence of the secondary structure

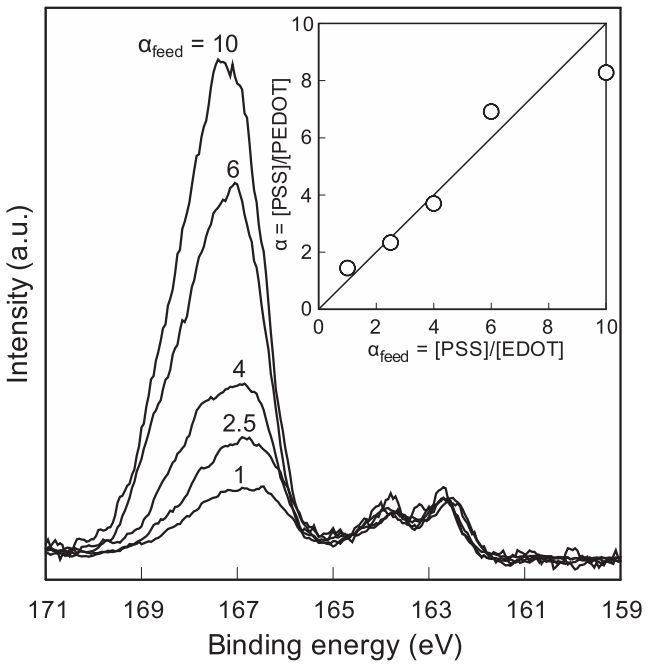

Fig. 1. XPS spectra of PEDOT:PSS with various feed composition ratios (α_{feed}) of PSS repeating unit to EDOT monomer in the energy range of the S 2p signal. Inset: Relation between α_{feed} and actual composition ratio (α) of repeating units for PSS and PEDOT estimated from the XPS spectra.