

Preparation and characterization of conducting poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) Langmuir–Blodgett film

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Abstract

The self-assembly of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) nanoparticles at an air/water interface was achieved by means of the electrostatic force between an octadecylamine (ODA) monolayer and PEDOT-PSS nanoparticles. A surface pressure (π)–area (A) isotherm and X-ray photoelectron spectroscopy of the composite film were used to confirm the electrostatic force between the SO_3^- group of PSS and the NH_4^+ group of aliphatic amines. Monolayer and multilayer composite films of ODA/PEDOT-PSS and ODA-stearic acid (SA)/PEDOT-PSS were fabricated. These solid Langmuir–Blodgett films were investigated by the UV–Vis spectrum, atomic force microscopy, and X-ray diffraction method. It is observed that ODA-SA/PEDOT-PSS films had a higher film-forming capability than ODA/PEDOT-PSS films and an ordered multilayer structure was developed. The conductive properties of ODA-SA/PEDOT-PSS LB films were investigated in detail. Factors influencing the film conductivity such as the layer number and surface pressure were discussed and the conductive mechanism was also studied.

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1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a promising conducting polymer that has excellent electrical conductivity and optoelectronic properties [1–5]. The solubility problem of PEDOT has been avoided by using a water-dispersible polyelectrolyte, poly(styrene sulfonate) (PSS); its use as a charge-balancing counterion in the doping polymerization yields poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS, as shown in Fig. 1). In the form of a colloidal dispersion, PEDOT-PSS is stable in water and can be used to conveniently form thin films by many methods [6–11]. Moreover, the ionization of PSS, which is a chemical dopant, demonstrates the possibility of developing an electrostatic self-

assembly film using this material, which offers a simple alternating adsorption of polyanions and polycations in order to develop a polyelectrolyte multilayer structure on charged substrates [12–14].

Langmuir–Blodgett (LB) and other film fabrication technologies based on electrostatic attraction self-assembly have been demonstrated to be useful for the immobilization of polyelectrolytes; the former is a promising method for developing artificial supermolecular assemblies [15–21]. Furthermore, the LB technique can provide a more uniform and highly ordered structure and the utilization of this method to deposit films of electroconductive materials shows enormous potential for applications in electronic devices and microdevices [22–25]. Nanoparticles of PEDOT-PSS can disperse thoroughly in an aqueous solution and charged PSS can be electrostatically adsorbed on an ionization monolayer, which indicates the feasibility of applying electrostatic self-assembly by the LB technique to obtain a highly ordered structure.

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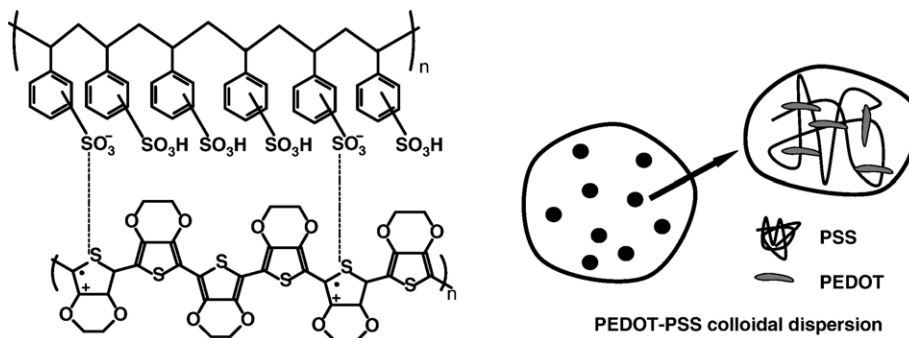


Fig. 1. Molecular structure of PEDOT-PSS and schematic illustration of PEDOT-PSS colloidal dispersions.

In this paper, we report a method to immobilize PEDOT-PSS nanoparticles by the LB inducing technique. The low film-forming ability of an octadecylamine (ODA)/PEDOT-PSS film was avoided by spreading a mixed ODA-stearic acid (SA) monolayer on a subphase containing PEDOT-PSS nanoparticles. An ordered layer-structure ODA-SA/PEDOT-PSS LB film was obtained through the conventional vertical LB dipping mode. The composite LB films were investigated using the UV–Vis spectrum, atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) methods. We also conducted a detailed investigation of the film conductive performance such as conductivity and direct current (DC) current–voltage (I – V) characteristics. The mechanism of the conductive performance of composite LB films was also discussed.

2. Experimental details

A blue aqueous colloidal dispersion of PEDOT-PSS (Baytron P) was purchased from Bayer AG. ODA, SA and other chemical reagents were purchased from Aldrich and used as received.

The subphase solution was prepared using ultrapure water (resistance $> 18 \text{ M}\Omega$, $\text{pH}=5.1$). The subphase solution containing PEDOT-PSS nanoparticles was first pretreated in an ultrasonic bath for 15 min and filtered using a $0.45\text{-}\mu\text{m}$ filter (millipore, poly(vinylidene fluoride)), following which it was transferred into the LB trough. Surface pressure–area (π – A) isotherm measurements and deposition experiments were performed using a computer-controlled KSV-5000 instrument (Finland). A 70-ml chloroform solution of 0.5 mg/ml ODA or a chloroform solution of mixed ODA-SA (2:1) was spread on an aqueous subphase containing PEDOT-PSS. After the thorough evaporation of the solvent for 30 min followed by the electrostatic adsorption of PEDOT-PSS onto the ODA monolayer, the floating layer on the subphase was compressed at 1 mm/min and the π – A isotherm was recorded simultaneously. After an appropriate surface pressure was obtained, the monolayer was compressed for 30 min under an oscillation mode with a speed of 0.5 mm/min. It was then easily transferred onto the substrate using the vertical dipping mode and the transfer ratio (TR) was found to be approximately 0.85–0.95.

In order to study the absorbance characteristic, the film was deposited on a quartz substrate and measured using a DT-1000CE spectrometer. In order to investigate the surface morphology, the film was deposited on an indium–tin oxide (ITO) substrate and

investigated using AFM in the tapping mode (Model SP 3800, Seiko Instruments Inc., Japan) with a standard tip. The horizontal electrical conductivity ($\sigma_{//}$) of composite films was measured by a four-point probe method. An ITO/LB film/Au-sandwiched structure was fabricated in order to investigate the perpendicular conductivity (σ_{\perp}) and DC I – V characteristic of the composite LB films; the experiment was carried out in a Keithley 4200 semiconductor testing system in air at ambient temperature. The film thickness was measured by using a spectroscopic ellipsometer (SENTECH SE850, Germany). The LB film for XPS investigation was deposited on a hydrophobic silicon substrate. This investigation was conducted using a Scienta ESCA200 spectrometer. The X-ray source used was an $\text{AlK}\alpha$ radiation (1486.6 eV, non-monochromatic) anode operated at 14 kV and 20 mA. The photoelectrons were collected at an electron take-off angle of 50° and were analyzed based on their kinetic energies with a pass energy of 50 eV. The measurements were made at room temperature under a pressure of 3×10^{-7} Pa in a test chamber. The energy shifts caused in the spectra due to surface charging during the measurements were corrected by using the C (1s) level (284.8 eV) of the adventitious carbon on the sample surface as an internal standard. The XRD analysis of the film structure was performed on a DRON2 diffractometer by a symmetrical coupled $\theta/2\theta$ step scanning using $\text{CoK}\alpha$ radiation at ambient temperature.

3. Results and discussion

The π – A isotherm of ODA and mixed ODA-SA monolayers spread on pure water and a subphase containing PEDOT-PSS nanoparticles was investigated, and the result is shown in Fig. 2. It shows that both ODA and mixed ODA-SA monolayers have a larger molecular area on a subphase containing PEDOT-PSS nanoparticles than that on a pure water subphase and a stable composite film is formed at the air/water interface. The average molecular areas of these films are 0.3, 0.5, and 0.2 nm^2 , respectively. The composite Langmuir films are stable at the air/water interface and have a collapse pressure as high as 50 mN/m. This phenomenon is ascribed to the intense electrostatic force between the SO_3^- group of PSS and the NH_4^+ group of aliphatic amines, which results in the adjacent charged PEDOT-PSS nanoparticles at the monolayer that repel each other and induce the expansion of the monolayer. We observed a distinct

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