

Molecular assembled self-doped polyaniline copolymer ultra-thin films

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Abstract

A self-assembly technique and copolymerization were used to buildup a self-doped polyaniline (SPANI) ultra-thin film on an indium-tin oxide (ITO) substrate. The monomers used were aniline and its derivative MSAN (*m*-aminobenzenesulfonic acid). Successful MSAN/AN copolymerization and film formation were simultaneously performed in aqueous solution with the addition of oxidant (APS, ammonium persulfate). The film deposition rate of a high AN/MSAN ratio system is generally higher than that of a low AN/MSAN ratio system. Cyclic voltammetry, UV–vis spectroscopy, and α -step instruments indicate a systematic dependence of the film thickness of these ultra-thin films on the assembly time and temperatures. The Auger depth profile reveals the elemental distribution in these films and exhibits different deposition rates between AN and MSAN. XPS N_{1s} spectra also show the variation of the degree of doping. This SPANI film can be used as an electrochromic electrode in a corresponding device. Carboxyl-terminated-butadiene-acrylonitrile (CTBN) blended with LiClO₄ was used as a solid polymer electrolyte. A total solid electrochromic device was assembled as ITO/SPANI/LiClO₄–CTBN/PEDOT:PSS/ITO, where PEDOT:PSS is poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) as the counter complementary electrode. The device was pale gray at –1.5 V and blue at +1.5 V.

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1. Introduction

Conducting polymer is a promising material for further applications in molecular electronics, molecular wires, and devices [1,2]. Polyaniline (PANI) is the simplest linear conjugated macromolecule and a representative of conducting polymers [3]. To combine two or more desirable properties, multicomposites can provide additional stability for molecular assembly. Even fine device functionality will result from a combination of physical and chemical processes (e.g., electron and energy transfer). Such a device requires control of

molecular orientation and organization on the nanoscale, because its function significantly depends on the local chemical environment. Therefore, scientists greatly desire to develop methods for the controllable assembly of multicomponent nanostructures.

Single molecular layers can be consecutively deposited onto planar solid supports and then form multilayers in which organic molecules can be controlled in at least one dimension with nanoscale arrangements. This process clarifies a fixed relation between nanoscopic order and macroscopic orientation to develop functional macroscopic devices. To fully exploit an assembled structure, it is necessary to know the location or orientation of the molecules [4]. In these systems, the molecularly controlled fabrication of monolayer films has been

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dominated by the Langmuir–Blodgett (LB) technique [5]. Monolayers are formed on a water surface and then transferred onto a solid support. The LB technique requires special equipment and has severe limitations in substrate size and topology as well as in film quality and stability. Since 1980s, self-assembly techniques have been developed as an alternative to LB films in a silane–SiO₂ interface [6], metal phosphonate chemistry [7], as well as ultra-thin films of Zener diodes from conducting polymers and CdSe nanoparticles [8]. Based on covalent and coordination chemistry, self-assembled films are restricted to certain classes of organics, and high-quality multilayer films cannot be reliably obtained. These problems mainly arise from the high steric demand of covalent chemistry, which is a prerequisite for remaining functional group density in each layer.

Recently, the layer-by-layer polyelectrolyte (such as polyanion and polycation) deposition route has been developed for the fabrication of ultra-thin polymer layers [9–11]. Using this route, the incorporation of ultra-thin (<100 Å) charge-injection interfacial layers in polymer light-emitting diodes [12] has been achieved. Polycations and polyanions are alternately adsorbed from their respective solutions onto the substrate to form a multilayer film in which the thickness and other physico-chemical properties of the sub-layers can be tuned over molecular widths [9–12]. A strong cooperative ion-pair interaction locks the chain segments into highly interpenetrated structures [9–12] to buildup a multilayer film at the molecular level. Here we fabricated the thin film of self-doped polyaniline on an indium-tin oxide (ITO) substrate. It was desirable to create a simple approach that would form uniform nanoarchitecture films, whereas the fabrication was expected to be independent of the nature, size, and topology of the substrate. The electrostatic attraction between oppositely charged molecules (such as propagating molecule chains) seemed to be a good candidate as a driving force for film buildup, because it possesses the least steric requirement of all chemical bonds. Strong electrostatic attraction occurs between a charged surface and oppositely charged molecule in solution. This phenomenon has been known for the adsorption of small organics and polyelectrolytes [13], but it has rarely been studied with respect to the film formation of propagating conducting polymers. The formation of self-doped polyaniline ultra-thin films has important consequences for flocculation and is therefore of interest in large-scale processes such as charge-injection layers in polymer light-emitting diodes [12] and electrode materials in electrochromic device [2]. However, this process is considered to be an alternative method to fabricate uniform thin films. These applications may benefit from a better understanding of self-doped polyaniline films as model systems, as these can be well characterized by a wide variety of physical techniques.

In this work, aniline (AN) was dissolved in an aqueous solution of *m*-aminobenzenesulfonic acid (MSAN). MSAN was used as a monomer, a surfactant, and a self-dopant. Then, ammonium persulfate (APS) was added as the oxidant. A series of ultra-thin films were visually observed during the assembly.

2. Experimental section

2.1. Chemicals

Aniline (Merck) was distilled under reduced pressure. *m*-Aminobenzenesulfonic acid (Acros) was purified by recrystallization two times from distilled water using the method of our previous work [14]. Oxidants (ammonium peroxydisulfate (APS), Wako), lithium perchlorate (LiClO₄, Merck), carboxyl-terminated-butadiene-acrylonitrile (CTBN, Hycar 1300× 8), and poly(3,4-ethylenedioxythiophene) (PEDOT)–poly(4-styrenesulfonate) (PSS) (Merck) were used as received. The ITO-coated glass substrates ($\sim 10 \Omega \text{ cm}^{-2}$, Merck) were first cleaned by a mixture of H₂O/H₂O₂/NH₃ with the ratio of 10:2:0.6 at 55–60 °C for 1 h. The substrates were baked in a vacuum (165–170 °C, 150 min) to remove physisorbed water and followed by UV–O₃ irradiation for 20 min.

2.2. Self-assembly of SPANI ultra-thin films

Aniline and MSAN (total –NH₂ concentration kept at 0.057 M) were dissolved in 100 mL of distilled water with a desired AN/MSAN mole ratio ranging from 0.25 to 4.0. Far from the intervals, the experiments were difficult to perform. The solution was magnetically stirred at a specific reaction temperature (4–25 °C). An aqueous solution of (NH₄)₂S₂O₈ (0.57 g) with a 12.5 mL volume was added to the above monomer mixture in one portion at the same temperature. The resulting solution was stirred for another 2 min to ensure complete mixing. To develop a film of SPANI as illustrated schematically in Fig. 1, SPANI-based ultra-thin

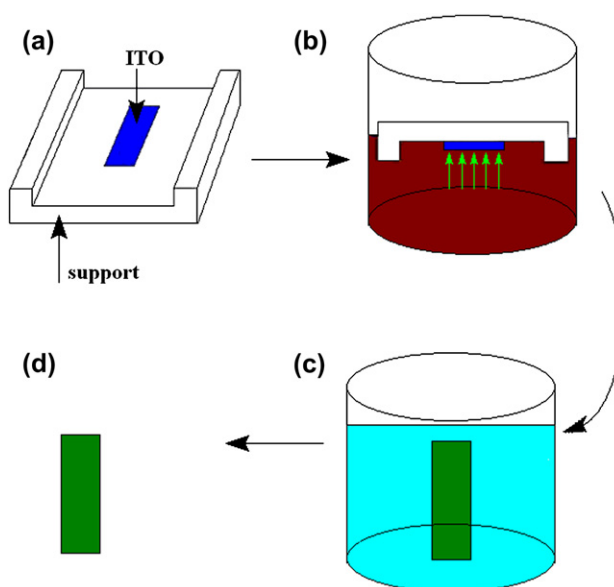


Fig. 1. Schematic of the SPANI film deposition process employed an immersing self-assembly method. Step a represents the fixing of the ITO glass onto a support. Step b is the deposition of a SPANI film in the reaction solution, and steps c and d are washing and drying steps, respectively. The four steps are the basic buildup sequence for an ultra-thin film of SPANI. Chemical components in the reaction solution have aniline, *m*-aminobenzenesulfonic acid, ammonium peroxydisulfate, and water.

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