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Highly controllable ambient atmosphere spray deposition of water dispersible poly(benzimidazobenzophenanthroline) films

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ABSTRACT

Thin films of water dispersible poly(ethylene oxide) (PEO) functionalized poly(benzimidazobenzophenanthroline) (BBL) polymers have been prepared by a pulse spray technique on a spinning substrate in ambient atmosphere. The deposition method is advantageous for generating ultra-thin films of nanometer thicknesses. A single spray pulse was found in a reproducible manner to generate a layer of ca. 2 nm thickness. The PEO-chain length in the BBL functionalization had an essential influence on the building mechanism of the films. The polymers functionalized by short PEO chains induced the formation of very smooth films while longer PEO chains induced rough films and notable nanostructuration. The BBL-PEO film deposited using spray pulse deposition was found to be electro- and photoactive. The electron transfer processes observed are slightly different from earlier reported results for similar polymers, which is probably due to the very thin film. The films exhibited photocurrent generation when transformed into conducting form.

1. Introduction

Poly(benzimidazobenzophenanthroline) (BBL) is an aromatic ladder-type conjugated polymer which has been synthesized already in late 1960's [1,2] and has since then been actively studied [3–7]. The BBL's molecular structure is planar due to its rigid backbone and possesses high chemical and thermal stability [8] as well as high electron affinity [9]. BBL can be utilized as an n-type conducting film in for example optoelectronic devices, where there is a demand for stable n-type organic semiconductors [10]. The use of BBL in photovoltaics and organic transistors is already reported in literature [11–22]. Previously BBL was proven an effective photoanode material for water oxidation [23].

Organic materials have been used progressively in electronics (solar cells, OFETs, OLEDs, etc.). The deposition processes of thin organic films when utilized in devices highly affects the function of the device. In order to improve device performance, there is a need of new approaches to deposit films of high homogeneity and precise thickness control. Advanced thin film devices are essentially multilayer structures where all layers should be processed without affecting the underlying layers, which remains a challenge in multilayer assemblies. On the other hand, devices consist of multilayer structures where each layer in the stack can be conveniently deposited by an individual technique. Spin-coating persists the most widely used liquid phase deposition technique. Nevertheless, the method cannot be used for large area devices and there are problems when the multilayered materials are soluble in the same solvents. Furthermore, the lack of control at nanoscale is usually considered as a major drawback in liquid phase deposition. One approach to conquering the problems is chemical vapor deposition and atomic layer deposition [24]. These rather expensive methods consume a lot of energy per deposited material, have slow growth rates and utilize custom-made precursor molecules. On the other hand, they usually ensure error free epitaxial growth in the atomic level with strong bonds between the molecules. Conducting polymer films are traditionally assembled via electrochemical deposition. However, the method is not applicable to BBL due to lack of appropriate monomer. Another significant drawback in the utilization of BBL is insolubility, as such, in practically any common solvent. Methanesulfonic acid is an exception, which has been found to dissolve BBL [9]. The methanesulfonic acid solution can be transformed into an aqueous nanofiber dispersion, which can be utilized in preparation of thin BBL-films [23,25,26]. In addition, stable dispersions and high colloidal stability in aqueous solutions can also be achieved by substituting poly (ethylene oxide) (PEO, Scheme 1) [27] and poly(N-isopropylacrylamide) [28] in

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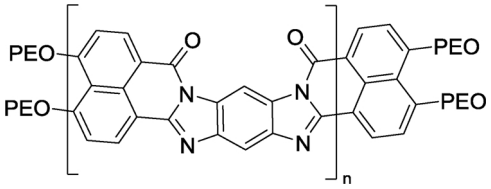

Scheme 1. Common structure of poly(benzimidazobenzophenanthroline)- poly (ethylene oxide) (BBL-PEO) polymers used in this paper.

the chain ends of BBL. The PEO substitution does not significantly alter the electrical and optical properties of BBL [6]. Furthermore, the substitution facilitates the processability in water dispersion, which can be utilized in straightforward thin film deposition. BBL-PEO has been shown to be suitable for composite material formed with a p-type polymer [29].

We have previously constructed a deposition system where spraying is applied onto a substrate during high-speed spinning [30]. Spraying allows very fast wetting of the surface of a substrate with a minimal amount of solution, even less than what is used in a single step of spin coating. In a spinning motion, the draining and drying of the substrate is promoted by centrifugal force. Therefore, very rapid successive spray steps are then possible. Centrifugal force also minimizes the effect of surface tension so the drop boundaries, which are sometimes considered problematic in spraying applications, are not observed in high speed spinning substrate [30]. In this paper we utilize a deposition of water dispersible BBL derivatives using short aerosol pulses sprayed towards a spinning substrate. The aim of this approach is to obtain smooth, defect-free and uniform thin BBL films using inexpensive, vacuum-free process that is applicable to multilayer assemblies.

2. Experimental section

2.1. The substrates and materials

The substrates (quartz plates (Alfa Aesar), silicon wafers and fluorine doped tin oxide glass (SnO_2, K Glass from Pilkington)) were cleaned using H_2O_2:NH_3:H_2O (1:1:5) solution, rinsed with water, dried, and silanized using a 5% (v/v) solution of *N*-(trimethoxysilylpropyl)-*N,N,N*-triethylammonium chloride (ABCR) in methanol for 5 min. The BBL-PEOs used were synthesized earlier and the detailed synthesis and characterization is described elsewhere [27]. BBL derivatives were used as 1.5 mg/ml water dispersions. Before deposition, the dispersions were homogenized for 15 min using a tip sonicator (Hielscher UP100 H). After that, the dispersions were centrifuged for 15 min in 3000*g* for separating remaining aggregated particles.

2.2. The spraying system

The spraying system (Fig. 1) constituted of on house made air-atomizing nozzle made of polytetrafluoroethylene (PTFE). The air channel inside the nozzle was 2 mm and polyether ether ketone (PEEK) tube (1.6 mm outer diameter) for liquid feed was fitted inside the air channel. The nozzle was driven with 200 kPa pressurized air. The liquid was pushed from the container using 30 kPa overpressure in order to achieve a steady liquid flow. A uniform spray cone was generated by opening the solenoid valve (NResearch) after the liquid container while the air was constantly driven through the channel. A single spray pulse for the duration of 100 ms consumed ca. 35 µl of solution. Drying of the spinning substrate took place within one second, but for repeatability, a five-second delay was kept in between the successive pulses. Spraying time was controlled using LABVIEW software (National Instruments) and the interface board (National Instruments USB-6008). Spraying was applied on a substrate attached to the spinner (Pine instrument company) having adjusted spinning speed of 5000 rpm. After the deposition, the BBL films were annealed at 70 °C for one hour.

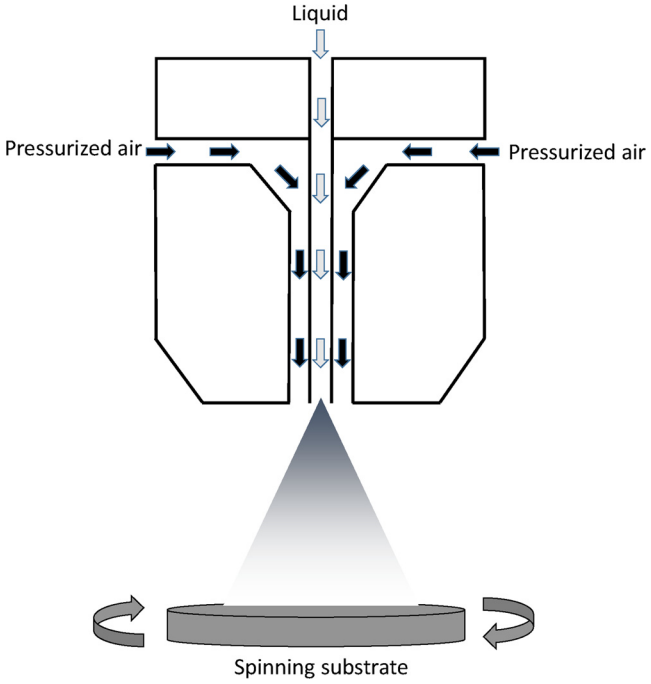

Fig. 1. Scheme of the spraying nozzle.

2.3. Characterization of films

The UV–vis spectra were measured by HP 8453 spectrometer. Atomic force microscopy, AFM (diCaliber AFM, Bruker), operated in the tapping mode was used to measure the topography and the root mean square roughness of each film deposited on silicon. The films were also scratched with a doctor blade in order to get an estimate of the film thickness. The morphology of the films was also studied by scanning electron microscopy, SEM (LEO Gemini 1530)

The ellipsometric analysis of a polymer film on silicon was carried out using EP3 spectroscopic and imaging ellipsometer (Accurion). Xe lamp was used in the spectral range of 370–950 nm. The ellipsometric spectra were analyzed using EP4Model modeling software (Accurion) with the following optical model: Si/SiO_2/BBL/BBL(rough). Tauc-Lorentz model [31] was used in modeling BBL and Bruggemann effective medium for modeling rough surface layer.

Electrochemical characterization was carried out in a conventional three-electrode one-compartment cell using cyclic voltammetry (CV) and an Iviumstat potentiostat. The cell was filled with 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The working electrode for CV experiments was FTO coated glass and a platinum wire was used as a counter electrode. An AgCl coated Ag wire was used as quasi-reference electrode and all potentials reported are vs. this electrode. The Ag/AgCl electrode was calibrated vs. ferrocene (Fe/Fe^+) ($E_{1/2}$ (Fe/Fe^+) = 0.45 V) before each experiment

Photocurrent generation in the thin films were studied using white LED and 590 nm LED illumination (Ivium ModuLight) having power densities of 16 mW/cm^2 and 1.6 mW/cm^2 respectively measured with a calibrated photodiode. The illumination was carried out from the backside of the glass plate using the same three-electrode cell filled with the same electrolyte solution as in CV measurements. The system was analyzed in forward bias and in an open circuit mode. To rule out possible interferences a blank FTO-glass plate with electrolyte solution was analyzed by light on-light off measurement.