

Fabrication of Organic Photovoltaic Devices by the Layer-by-Layer Polyelectrolyte Deposition Method

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Abstract— Organic photovoltaic cells were fabricated by the layer-by-layer polyelectrolyte deposition process by which the film thickness can be controlled accurately. Ruthenium/rhenium complexes containing poly(*p*-phenylenevinylene) and sulfonated polyaniline were used in the process. This new method provides flexibility in the fabrication of multilayer polymeric devices with well-defined structure.

Keywords-component: photovoltaic, organic polymers, transition metal complexes

I. INTRODUCTION

There has been an increased attention in the use of organic polymeric materials for photovoltaic cells [1]. Organic polymers enjoy the advantages that they can be fabricated into large area devices with high flexibility. The physical properties of the polymers can also be easily tuned by structural modification. In organic photovoltaic devices, the excitons are quenched easily and have limited diffusion length. Therefore, controlling the thickness of the sensitizing and charge transport layers is essential. Most of the polymer-based multilayer heterojunction or bulk heterojunction photovoltaic devices were prepared by blending the polymer solution with a dopant, which is then spin coated on a substrate. The thickness of the device was controlled by adjusting the spinning speed and the concentration of the polymer solution. However, it is difficult to control the polymer film thickness, and ultrathin film (< 10 nm) is very difficult to obtain. In order to optimize the film thickness and spin coating condition, a lot of experimental work is required.

Layer-by-layer electrostatic self-assembly was developed by Decher in early 90's for the preparation of ultrathin polymer films [2]. It involves the alternate deposition of oppositely charged polyelectrolytes. This technique is simple, versatile, and fast compared to other traditional film forming techniques. It was used in the fabrication of sensors [3], erasable ultrathin polymer films [4], electroluminescent devices [5], and patterned microstructures [6]. More recently, this technique was extended to the fabrication of photodiodes. Here, we report a new fabrication method of preparing polymeric photovoltaic cells by the layer-by-layer polyelectrolyte deposition [7]. By

alternative deposition of a photosensitizing polymer and a charge transport polymer, the sensitizer can be embedded into a conducting matrix and the thickness of the thin film can be controlled accurately by the number of bilayers deposited. Two different metal complex containing conjugated polymers were used in the study. These photosensitizing polymers are based on poly(*p*-phenylenevinylene) (PPV) main chain on which with bis(2,2':6',2''-terpyridine) ruthenium(II) [8] or chlorotricarbonyl rhenium(I) aromatic diimine complexes [9] are attached. Their structures are shown in Figure 1. These polymers are co-deposited with sulfonated polyaniline (SPAN) on an ITO substrate to give photovoltaic devices with the structure ITO/(metal-containing polymer/SPAN)_n/Al. When the devices were irradiated with AM 1.5 simulated solar light, the power conversion efficiency was measured to be in the order of 10⁻³ %. The performance can be improved by incorporation of other n-type polyelectrolytes, or by optimization of device thickness. The method provides a new approach in fabricating polymeric multilayer photovoltaic devices with predefined structure and thickness.

II. EXPERIMENTAL

A. Synthesis of Polymers

The ruthenium-containing PPV (Ru-PPV) and rhenium-containing PPV (Re-PPV) were synthesized by the palladium catalyzed Heck coupling reaction using the general procedure published previously [10]. Sulfonated polyaniline (SPAN) was synthesized according to literature procedure [11]. The structures of the polymers are shown in Figure 1.

B. Fabrication of Thin Films

Photovoltaic devices with the structure ITO/(Ru-PPV/SPAN)_n/Al were fabricated by dipping the ITO glass into solutions of Ru-PPV in DMF and SPAN in water. The indium tin oxide (ITO) glass substrates used in the studies were pre-treated with (3-aminopropyl)trimethoxysilane prior to use. The ITO glass slides (Samsung Electronics, South Korea) with a surface resistivity of 20 Ω/□ were cleaned sequentially by Decon 90 (Decon Laboratories Ltd., detergent for ITO

substrate), distilled water, acetone, distilled water, ethanol, distilled water, methanol, methanol/toluene (1:1), and then toluene. The glass slides were then immersed in 5 wt. % (3-aminopropyl)trimethoxysilane in toluene for 16 h to introduce amine groups on the glass slides surface.

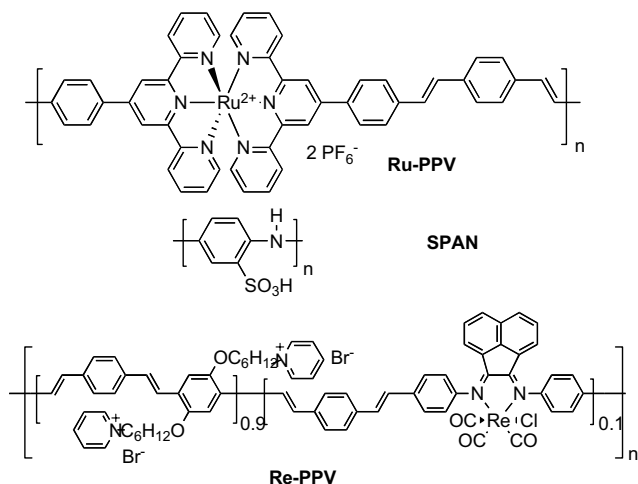


Figure 1. Structures of the polymers

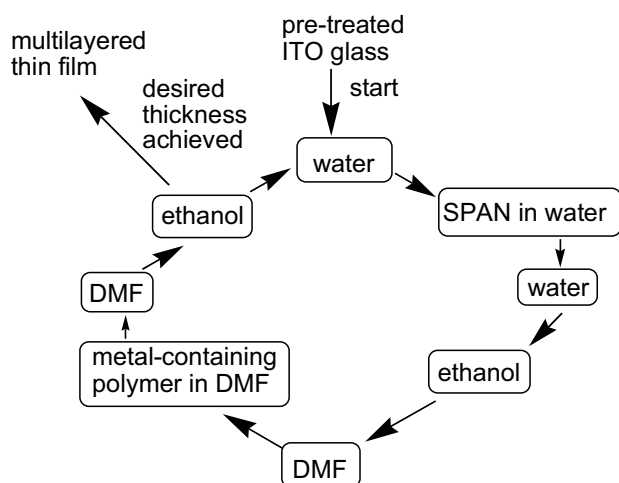


Figure 2. Schematic diagram showing the deposition process.

For the layer-by-layer deposition process, the pretreated ITO glass was immersed in the metal-containing polymers solution (0.1 mM in N,N-dimethylformamide DMF) and SPAN solution (0.1 mM in water) in sequence. Between each dipping process, the glass slide was rinsed with different solvents in order to prevent the precipitation of polymer on film surface. The time for dipping in polyelectrolyte solutions was 7-15 minutes. The rinsing time was kept at 2 minutes for each solvent. This process was repeated until the desired number of bilayers was achieved. The deposition process started from immersing the ITO substrate into distilled water, and in the sequence of **SPAN** (0.1 mM), distilled water, ethanol, DMF, **Ru-PPV** or **Re-PPV** (0.1 mM), DMF and ethanol. The schematic diagram of the whole process is summarized in Figure 2. Apart from the two polymer solutions, other solvents

were used for rinsing the substrate. After each cycle the substrates were dried by a blowing air stream for 30 secs. For the thin film used for morphological study, they were fabricated on pretreated glass slide using the same dipping method. Thin films with different number of bilayers were prepared. On the polymer film surface, a layer of aluminium electrode was coated on the film surface.

The photovoltaic properties of the devices were studied by irradiation with AM 1.5 simulated solar light and the current voltage characteristics of the devices were measured with a Keithley 2400 source meter. The surface morphology of the thin films was studied by Atomic Force Microscopy on a Digital Instruments Nanoscope IIIA.

III. RESULTS AND DISCUSSION

A. Surface Morphology

In order to study the effect of solution pH on the surface morphology of thin films, thin films with 20 bilayers were prepared by SPAN solutions with different pH.

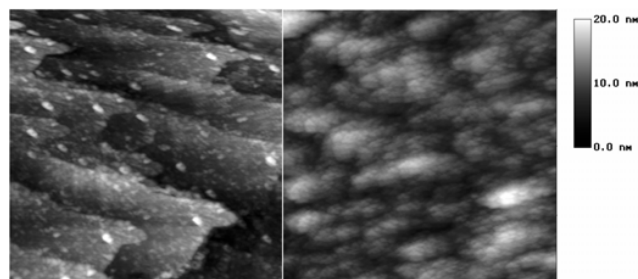


Figure 3. Tapping mode AFM images for ITO/(SPAN/Ru-PPV)₂₀ prepared in acidic SPAN (left) and basic SPAN (right). (size 1 μm by 1 μm)

The AMF images of the films were shown in Figure 3. The aggregation on the surface for the basic SPAN image is quite small, with the size less than 50 nm. The roughness (root mean square) of the film is 2.4 nm. The overall surface morphology is even throughout the film. For the thin film prepared in acidic SPAN, larger aggregates were observed on the surface. The roughness of the film is 2.9 nm.

B. Photovoltaic Properties

Both ruthenium and rhenium containing poly(p-phenylenevinylene)s exhibit photosensitizing properties, they were employed as the photosensitizing layer in solar cells. The solar cells were prepared by layer-by-layer electrostatic self-assembly deposition method. The current-voltage characteristics of some of the films are shown in Figures 4 and 5. In the Ru-PPV system, the I_{sc} , V_{oc} , FF and η_p are 4.52 $\mu\text{A}/\text{cm}^2$, 0.28 V, 0.21 and $2.6 \times 10^{-4} \%$ respectively. In the Re-PPV system, the I_{sc} , V_{oc} , FF and η_p are 5.76 $\mu\text{A}/\text{cm}^2$, 0.36 V, 0.16 and $3.4 \times 10^{-4} \%$ respectively. Non-zero dark current was detected in the devices. This may be due to the presence of counter ions in the devices. During the thin film fabrication, counter ions in the polymer solutions would also become attached to the films by electrostatic forces. The ions that were trapped in the polymer film could be removed during rinsing,

but those counter ions present in the film for balancing the charges on the polyelectrolytes could not be removed .

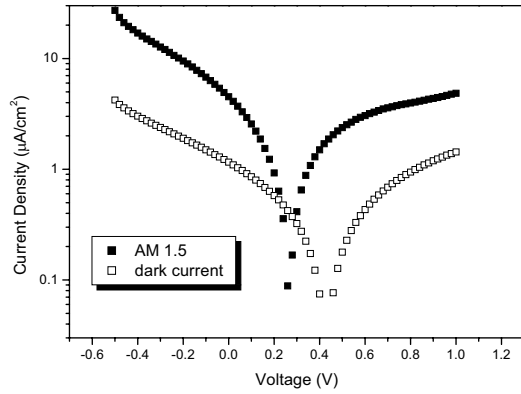


Figure 4. I-V characteristic of ITO/(SPAN/Ru-PPV)₄₀/Al device under AM 1.5 illumination.

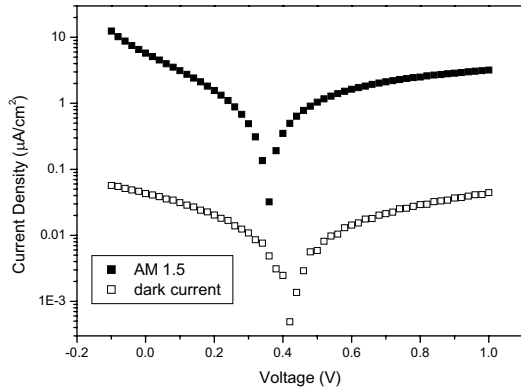


Figure 5. I-V characteristic of ITO/(SPAN/Re-PPV)₄₀/Al device under AM 1.5 illumination.

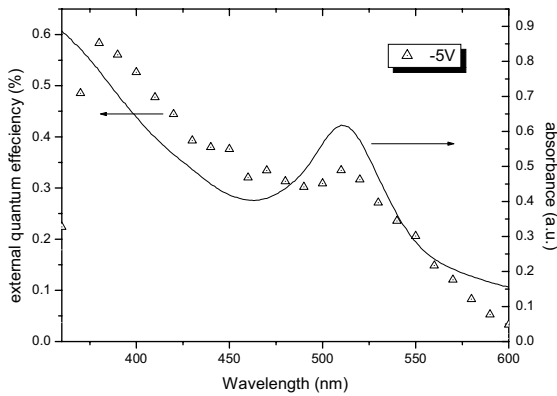


Figure 6. Plot of absorbance and external quantum efficiency under -5 V for the ITO/(SPAN/Ru-PPV)₄₀/Al device.

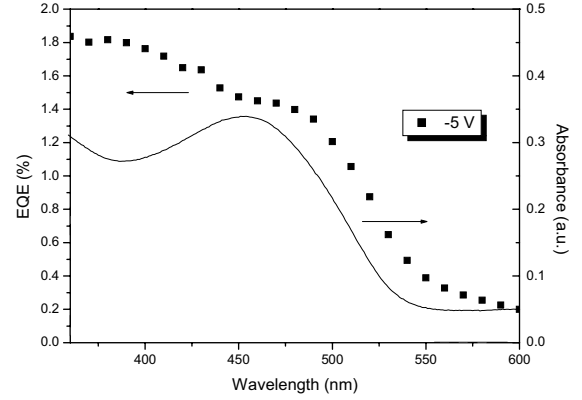


Figure 7. Plot of absorbance and external quantum efficiency under -5 V bias of the ITO/(SPAN/Re-PPV)₆₀/Al device.

The external quantum efficiency (η_{EQE}) is the primary parameter reflecting the fundamental detection and charge transport properties of the photovoltaic cell materials and structure. η_{EQE} is defined as the number of electrons flowing in the external circuit per photon incident on the PV cell (Eq.1)

$$\eta_{EQE} = \frac{I_{sc}}{eN_o} \quad (1)$$

where N_o represents the number of incident photons at particular wavelength and e represents elementary charge.

Figures 6 and 7 show the absorbance and external quantum efficiencies of the two photodetectors. η_{EQE} for the Ru-PPV system at 510 nm and Re-PPV system at 460 nm were measured to be 0.33 % and 0.36 % respectively. Due to the low absorbance of the device, η_{EQE} was relatively low since the efficiency is dependent on both photon absorption and exciton diffusion as $\eta_{EQE} \sim \eta_A \eta_{ED}$. The poor solar cell performance may be due to the relatively low carrier mobility of SPAN. In addition, the photovoltaic cell performance can also be greatly affected by the morphology of polymer film, which is strongly dependent on the film forming process. Therefore, further investigation in the deposition conditions and their effect to polymer morphological is required. The development of photosensitizing polymers with higher absorption coefficient is another approach in improving the device performance. By proper selection of photosensitizing materials, other spectral ranges such as near infrared and UV can also be detected. The photosensitizing region could be broadened by proper selection of materials. Metal-containing polymers are good candidates for photodetectors as the energy levels of the polymers can be fine tune easily.

IV. CONCLUSION

Ruthenium and rhenium containing conjugated polymers may act as photosensitizing materials in the solar cells fabricated by layer-by-layer electrostatic self-assembly deposition method. This preparation method provides multilayer thin films with relatively smooth surface morphologies and well-controlled thickness.

V. ACKNOWLEDGMENT

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VI. REFERENCE

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