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Communications

Efficient Photodetectors Fabricated from a Metal-Containing Conjugated Polymer by a Multilayer Deposition Process

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The emergence of organic semiconducting polymers for photovoltaic devices has opened a new area in designing new materials for energy conversion.[1,2] Organic polymers enjoy the advantages that they can be fabricated into large area devices with high flexibility. Besides, by systematically modifying the functional groups attached to the polymers, the sensitivity of the polymers can be easily tuned to a specific region (e.g., near-infrared). 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 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. However, it is difficult to control the thickness of the polymer thin film, and an ultrathin film ($<$10 nm) is very difficult to obtain. In addition, devices with multilayered structures are also difficult to fabricate because the solvent may dissolve the polymer already coated on the substrate.

Our group has been exploring the use of d^6 transition metal-containing conjugated polymers for optoelectronic applications because the complexes exhibit very interesting excited-state properties.[3,4] We previously showed that when bis(2,2′:6′,2″-terpyridine)ruthenium(II) complex was incorporated into poly(*p*-phenylenevinylene) (PPV) main chain, the resulting polymer exhibited enhanced photoconductivity in the visible region.[5] In addition, these types of metal-containing conjugated polymers can serve as both electron and hole transport materials with carrier mobilities on the order of 10^{-5} cm^2 V^{-1} s^{-1}.[6] Here, we report the fabrication of multilayer photovoltaic devices based on the ruthenium-containing PPV (**1**) and sulfonated polyaniline (**SPAN**, Figure 1) by the electrostatic self-assembly process. To the best of our knowledge, this is the first example of using dye-functionalized polyelectrolyte for photovoltaic cells. Layer-by-layer electrostatic self-assembly was developed to prepare ultrathin films.[7] It involves the alternate deposition of oppositely charged polyelectrolytes. This technique is simple, versatile, and fast compared to other traditional film-forming techniques.

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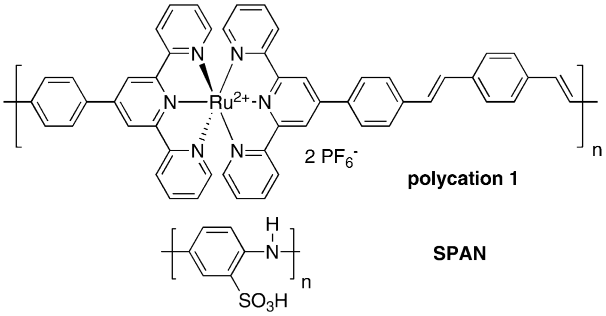

Figure 1. Structures of the polycation and polyanion used in deposition.

It was used in the fabrication of sensors,[8] erasable ultrathin polymer films,[9] electroluminescent devices,[10] and patterned microstructures.[11] More recently, this technique was extended to the fabrication of photodiodes.[12] However, the photosensitizing materials were mainly based on PPV, which was obtained from its precursor by thermal treatment after the polyelectrolyte thin film was prepared. The completeness of the thermal conversion was difficult to control and the choice of photosensitizing polyelectrolytes is very limited.

Polycation **1** was synthesized by the Heck reaction in good yield (95%).[4] **SPAN** was synthesized according to the literature procedure.[13] The photovoltaic devices were fabricated on indium−tin−oxide (ITO) glass pretreated with 3-aminopropyl trimethoxysilane.[14] A different number of bilayers composed of **SPAN** and **1** were coated on the substrate by sequential dipping of the ITO glass into solutions of **SPAN** (in water) and **1** (in DMF).[15] After a defined number of bilayers were coated, a layer of aluminum electrode (40 nm) was evaporated on the thin film under high vacuum. This method allows the deposition of alternating layers of hole transport (**SPAN**)[16] and electron transport (**1**) polymers. As a result, efficient hole and electron percolation pathways can be developed, which assist the exciton dissociation and charge transport processes after the formation of excitons. In addition, the thickness of the film can be reproduced accurately by controlling the number of bilayers. For the thin films with 13, 20, and 30 bilayers, the thicknesses were measured to be 110, 150, and 190 nm, respectively. It was previously reported that during the buildup of the first few layers, the polyelectrolytes were deposited on "conformationally" rough multilayers, and the thickness contributed from each bilayer would be significantly greater than those bilayers deposited subsequently.[17] Therefore, there was a decrease in bilayer thickness with the increase in number of layers. This effect will become less significant when the number of bilayers is increased further.

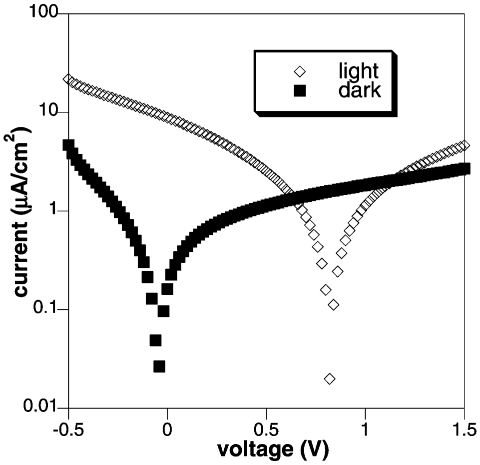

Figure 2. Current−voltage characteristics for the device ITO/(**SPAN**/**1**)$_{30}$/Al in the dark and under simulated solar light irradiation (63 mW/cm^2).

Table 1. Properties of Photovoltaic Devices with a Different Number of Bilayers (Incident Light Intensity = 63 mW/cm^2)

no. of bilayers	I_{sc} (μA/cm^2)	V_{oc} (V)	FF	η_p (10^{-3}%)	film thickness (nm)	film absorbance
13	15.0	0.84	0.16	3.2	110	0.13
20	12.6	0.78	0.18	2.8	150	0.19
30	8.9	0.76	0.20	2.1	190	0.43

Figure 2 shows the current−voltage characteristics of the device ITO/(**SPAN**/**1**)$_{30}$/Al under dark and illuminated with AM 1 simulated solar light at 63 mW/cm^2. ITO and Al serve as the anode and cathode, respectively. The short circuit current I_{sc}, open circuit voltage V_{oc}, fill factor FF, and power conversion efficiency η_p of the device were measured to be 8.9 μA/cm^2, 0.76 V, 0.20, and 2.2×10^{-3}% respectively. Table 1 summarizes the performance of devices with a different number of bilayers. It is interesting to note that although the device with 13 bilayers has lower absorbance, the I_{sc} measured was the highest. It may be due to the lower serial resistance. The values of FF and η_p of the devices are also similar.

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(13) Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665. With use of GPC with NMP as the eluent and polystyrene as the standard, the number average molecular weight and polydispersity of **SPAN** were measured to be 49 600 and 2.5, respectively.

(14) The ITO glass slides (Samsung Electronics, South Korea) with a surface resisitivity of 20 Ω/□ were cleaned sequentially by ultrasonicating in Decon 90 (Decon Laboratories Ltd.), distilled water, ethanol, water, methanol, methanol/toluene (1:1), and then toluene. The slides were then immersed in (3-aminopropyl)trimethoxysilane (5 wt % in toluene) under a nitrogen atmosphere for 16 h. The slides were then rinsed by untrasonicating sequentially in toluene, methanol/toluene (1:1), methanol, and then water. After drying in a vacuum oven, the slides were used for further deposition processes.

(15) The preparation of one bilayer involved the dipping of an ITO glass slide in different solutions for a certain time in the following sequence: water, **SPAN** in water (0.08 mg/mL), water, ethanol, DMF, **1** in DMF (0.09 mg/mL), DMF, and ethanol. The dipping time was 15 min for the two polyelectrolyte solutions and 2 min for each rinsing solvent. This process was repeated until the desired number of bilayers was achieved.

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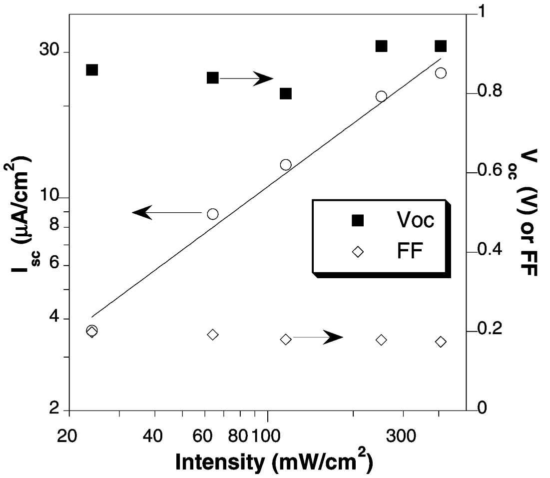

Figure 3. Dependence of the short circuit current, open circuit voltage, and fill factor of the device ITO/(**SPAN/1**)$_{30}$/Al on solar light intensity.

The dependence of I_{sc}, V_{oc}, and FF of the device ITO/(**SPAN/1**)$_{30}$/Al on irradiated light intensity is shown in Figure 3. I_{sc} was found to increase with light intensity as a power law $I_{sc} \propto (\text{intensity})^{0.70}$. This is similar to the case in other polymer/polymer blend photodiodes.[18] No saturation in current was observed within the intensity range. On the other hand, there was little change in V_{oc} and FF when the light intensity was increased. It was proposed that, in a donor−acceptor bulk heterojunction cell, V_{oc} was dependent on the acceptor strength.[19] In our polymers, the excitons have MLCT character and the nature of the acceptors are the same for all devices. Therefore, they exhibit similar open circuit voltage.

Figure 4 shows the photocurrent response of the device at different wavelengths under the bias of 0 and −5 V. The absorption spectrum of the device is shown for comparison. It can be clearly seen that the external quantum efficiency (η_{EQE}) of the device is maximum at ca. 510 nm with a value of 2.2%, and it agrees well with its absorption spectrum. This clearly shows that the enhancement is due to the presence of metal complex sensitizers. When the devices were subjected to a negative bias, an increase in η_{EQE} was observed. For the device with 30 bilayers, the maximum η_{EQE} was measured to be 5% at −5 V, indicating that the device can serve as a photodetector with a selective sensitization range. Due to the low absorbance, η_{EQE} is not very high since it is dependent on both photon absorption and exciton diffusion ($\eta_{EQE} \sim \eta_A\eta_{ED}$).[2] This can be improved by designing metal complexes with higher absorbance or by fabrication of thicker devices.

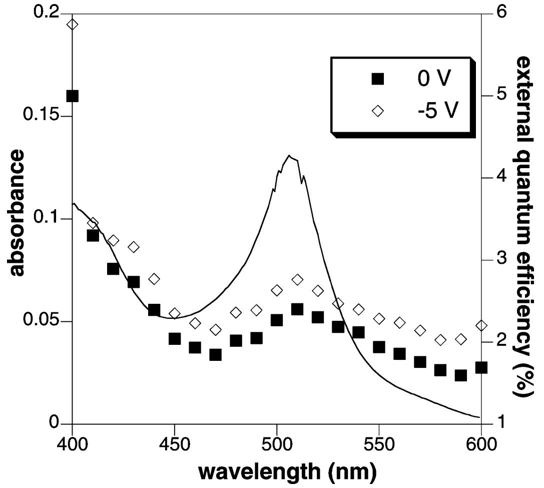

Figure 4. Plot of absorbance and external quantum efficiency (under 0 and −5 V bias) of the device ITO/(**SPAN/1**)$_{13}$/Al at different wavelengths.

In conclusion, the layer-by-layer deposition process is a simple and efficient method for fabricating photovoltaic cells/photodetectors in which the sensitization range is dependent on the metal-containing polycations used. The device thickness can be accurately controlled by varying the condition for the dipping process. Detailed studies in excitonic diffusion and charge transport are in progress. Since a variety of metal complexes can absorb photons of different energy, it is possible to prepare photodetectors with a wide range of photosensitivity by employing a mixture of metal complexes.

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