

Self-assembly of PPV/CdTe Nanocrystal Complex for Photovoltaic Device

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Abstract. This work focuses on studying a novel polymer/nanocrystal multilayer for the fabrication of donor and acceptor typed photovoltaic device. Highly luminescent anionic CdTe nanocrystals were prepared by aqueous synthesis method using 3-mercaptopropionic acid as stabilizer. The resultant CdTe served as electron acceptor and poly(p-phenylene vinylene) (PPV) was used as electron donor. Through the electrostatic interactions between cationic PPV precursor poly(p-xylylene tetrahydrothiophenium chloride) and anionic poly(sodium 4-styrenesulfonate) (PSS), PPV/PSS complex was fabricated on the surface of pretreated quartz substrate by layer-by-layer electrostatic self-assembly method. UV-Vis spectrum shows that PSS in the PPV/PSS complex make PPV precursors thermally convert into PPV at a lower temperature and less time. PPV/PSS/PPV/CdTe multilayer were fabricated on the surface of quartz substrate by electrostatic self-assembly method. The surface of the polymer/CdTe complex is flat, which was characterized by atomic force microscopy (AFM). UV-Vis spectrum of the polymer/CdTe complex shows that the absorbance increases with the increase of the number of deposition cycles. In the same way, PPV/PSS/PPV/CdTe multilayer were fabricated on the surface of ITO substrate disposed by the poly(3,4- ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). The resultant polymer/CdTe complex is measured under AM1.5G simulated solar illumination with $100\text{mW}\cdot\text{cm}^{-2}$ in air. The open circuit current density (V_{OC}) and short circuit current density (J_{SC}) of the polymer/CdTe complex are 0.60 V and $0.305\text{ mA}\cdot\text{cm}^{-2}$ which are better than PPV or CdTe nanocrystal individual. This could be ascribed to interfacial hole-electron converter between the conjugated polymer layer and CdTe nanocrystal layer. Besides, the photovoltaic properties of PPV/CdTe complex can be improved by controlling the layers of PPV/ CdTe nanocrystals complex on the ITO substrate.

Introduction

Polymeric and other organic materials as active components in photovoltaic devices have been widely researched due to their cheapness, lightweight, flexibility.^[1,2] However, the power conversion efficiency (PCE) of the heterojunction device has remained at the 1% level for a long time since the first report of thin-film organic solar cells by Tang.^[3] Recently the PCE is improved by application of the newly developed polymer/nanocrystal photovoltaic device owing to the high electron affinity of nanocrystals,^[4] the relatively low ionization potential of conjugated polymers and the compensated light harvest of nanocrystals and polymer. When the sunlight is absorbed by the hybrid device, the photo-induced excitons (electron-hole pairs) will be separated into free charges on the interface of the complex, and then transfer to both ends of device, but the exciton diffusion length is very limited.^[5] So it is very important to create more interfaces between polymers and nanocrystals and to control the device thickness that determines photocurrent and photovoltage. But the spin coating method which is most widely used to prepare photovoltaic device can not control molecular level interface architecture and film thickness accurately. Therefore, it is essential to find a substitute method to improve the photoelectric property of the polymer/nanocrystal photovoltaic device.

Layer by layer (LBL) electrostatic self-assembly method is the thin-film deposition technique by sequential absorption of oppositely charged polyelectrolytes that affords the control of molecular

level interface arrangement and film thickness.^[6] In this paper, the LBL method to prepare thin films of the PPV/PSS/PPV/CdTe complex in aqueous solution environment was studied. Poly-p-phenylene vinylene (PPV) and its derivatives were successfully used for light-emitting diodes (LEDs)^[7,8], solid-state laser, especially in photovoltaic devices because it shows an efficient photo-induced electron transfer in hybrid complex. Herein, PPV is replaced by cationic precursor PPV (pre-PPV) to fabricate the polymer/ nanocrystal LBL film owing to its water solubility. Anionic CdTe nanocrystals prepared by our lab are applied in the polymer/nanocrystal complex because of its proper bandgap for photovoltaic application and its absorption compensation for PPV.^[9] The key role of poly(styrene sulfonate) (PSS) played in the low temperature conversion from pre-PPV to PPV determines it as the counter ions to complement pre-PPV in the LBL preparation. This research may provide a thorough understanding for structure-property relationships of the PPV/CdTe complex. Moreover, it may even initiate a meaningful fabrication method for polymer/nanocrystal complex in the field of photovoltaics.

Experiment

Materials Pre-PPV (Aldrich, 0.25 wt %), PSS (Aldrich, Mw = 70, 000), CdTe (Self-prepared, particle size ~5nm)^[10], PEDOT:PSS (Aldrich, 1.3 wt%) were used without further purification.

Preparation of PPV/PSS/PPV/CdTe Layer-by-Layer Films Quartz substrates (12×32×1 mm³) were oxidized in Piranha solution for one hour and thoroughly rinsed with ultrapure water. ITO substrates (60×30×1 mm³, 10Ω square⁻¹) were cleaned by ultrasonication in ultrapure water, acetone, and isopropanol for 15 min each and dried with N₂ flow. PEDOT:PSS aqueous dispersion was spin-coated on the ITO substrate. The pretreated substrates were immersed alternately in the cationic pre-PPV solution (0.001M, pH = 8) and in the anionic CdTe dispersion or PSS solution (0.01M, pH = 8-9)^[11] for 10 min for each deposition, followed by 3 min of rinsing in ultrapure water. The substrates were dried under N₂ flow for 5 min after each immersion. Finally, the fabricated LBL films were annealed at 100°C for 2h under N₂ protection.^[12]

Measurements UV-vis absorption spectra were measured with a spectrophotometer (Agilent Co. Ltd., Agilent 8453). The surface morphology was measured by atomic force microscopy (AFM, Benyuan Co. Ltd., CSPM-4000) in the contact mode. The photovoltaic properties were measured by electrochemical workstation (Chenghua Co. Ltd., CHI660), using the prepared substrate as the working electrode, Pt wire as the counter electrode, and Ag/AgCl electrode as the reference electrode. The illumination was carried out by Xe lamp as the light source under AM 1.5G simulated solar irradiation at 100mW·cm⁻².

Results and discussion

Fig. 1 shows the UV-vis absorption spectra of PPV/PSS/PPV/CdTe (solid line) and PPV/CdTe/PPV (dashed line) annealing at 100°C for 2 hours. There is a transparent PPV character peak at 430 nm in the solid line ascribed to π - π^* absorption transition^[13] but a shorter flat plateau in the dashed line. The contrast illustrates that PSS plays a key role in the low temperature conversion from pre-PPV to PPV. Fig. 1 also shows the UV-vis absorption spectra of (PPV/CdTe)₃ film at 100°C for 2 hours (dotted line) and at 220°C for 11 hours (dash-dotted line). There is a narrow peak in the dashed-dotted line but not in the dotted line proved pre-PPV film without PSS have to be annealed at higher temperature and for longer time in order to convert to PPV completely. Although pre-PPV can be annealed into PPV at 220°C, for 11 hours, the PPV films need waste too much energy and high temperature will also enable the films form exciton or hole traps which go against the photovoltaic properties of the films. The low temperature conversion is ascribed to the substitution of chloride counter anions of pre-PPV with sulfonic anions of PSS.^[14] Compared to solid line, dash-dotted line is slightly blue shifted, which is associated with less inter-chain interaction of PPV because of the presence of inert PSS chains.^[15,16]

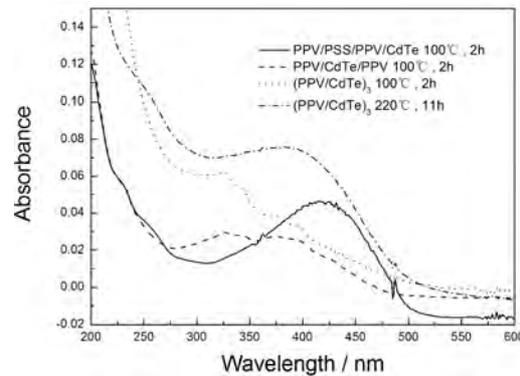


Fig. 1 UV-vis absorption spectra of PPV/PSS/PPV/CdTe (solid line), PPV/CdTe/PPV (dashed line), (PPV/CdTe)₃ at 100°C for 2h (dotted line), at 220°C for 11h (dash-dotted line)

We prepared (PPV/PSS/PPV/CdTe)_n (n=1, 3, 5, 7, 9) multi-films on the quartz substrates. (PPV/PSS/PPV/CdTe)₃ film is illustrated smooth and uniform with the roughness (root mean square) at 1.67 nm by AFM. Fig. 2 shows the UV-vis absorption spectra of (PPV/PSS/PPV/CdTe)_n multi-films. The absorbance at 430 nm increases with the increase of the number of deposition cycles. These results indicate the LBL method is effective to prepare this kind of polymer/nanocrystals complex and the similar amount is absorbed in each absorption cycle at fewer layers. But it is not easy to absorb more amounts on the films when the number of layers reaches 9. Therefore, there is no need to fabricate complex more than seven layers.

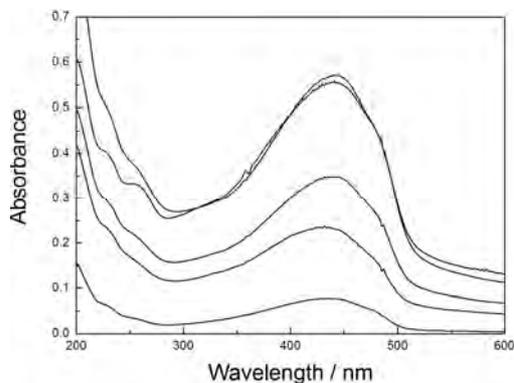


Fig. 2 UV-vis absorption spectra of (PPV/PSS/PPV/CdTe)_n film (n=1, 3, 5, 7, 9)

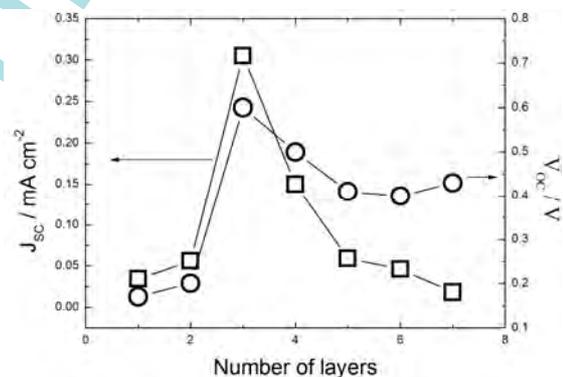


Fig. 3 Dependence of J_{SC} and V_{OC} on the number of (PPV/PSS/PPV/CdTe)_n multilayers

In order to further understand structure-photoelectric property relationships, we prepared seven films of (PPV/PSS/PPV/CdTe)_n complex (n=1-7), one film of (PPV/PSS/PPV/PSS)₃ and one film of (CdTe)₃ on the ITO substrates. Then the photoelectric properties were measured by electrochemical workstation under AM1.5G simulated solar irradiation with an intensity of 100mW·cm⁻² in air. Comparing the film of PPV/CdTe complex with CdTe and PPV/PSS films in the Tab.1, the J_{SC} and V_{OC} of PPV/CdTe complex are quite bigger than PPV/PSS and CdTe respectively. The improvement of J_{SC} should be mostly ascribed to the excitons separation between PPV and CdTe interface.^[17] Because the sequential layers are cross-linked,^[18] the separated excitons can transfer from interfaces to both ends without exciton recombination which can impact V_{OC} badly.^[19] As shown in Fig.3, all the seven films of multilayer complex exhibit favorable photoelectric performance. The maximum photovoltaic properties of the film were as follows: J_{SC} = 0.305 mA·cm⁻², V_{OC} = 0.60 V. because the increase of light harvesting layers can improve both the parameters, but too many layers will cause the increase of the film's resistance which decreases J_{SC} . Besides, V_{OC} decreases when the exciton diffusion length is exceeded by the film thickness so that excitons will trend to recombine^[20].

Table 1 Photovoltaic performance of multilayered film

Complex structure	$J_{SC} / (\text{mA} \cdot \text{cm}^{-2})$	V_{OC} / V
$(\text{CdTe})_3$	0.010	0.26
$(\text{PPV/PSS/PPV/PSS})_3$	0.140	0.48
$(\text{PPV/PSS/PPV/CdTe})_3$	0.305	0.60

Summary

In this study, we demonstrated layer-by-layer self-assembly deposition to prepare conjugated polymer/nanocrystals complex. The fabricated complex is flat, uniform and the absorption peak of PPV is at 430 nm. The absorbance amount of substance can be controlled. Introduction of PSS into PPV/CdTe complex ensures the low temperature conversion from pre-PPV to PPV. According to the photovoltaic properties of fabricated complex, we drew important conclusions on the complex physics and design rules. PPV/CdTe complex is better than respective PPV and CdTe as the interface effect of complex and the exciton pathways from interface to both ends. The multilayer PPV/PSS/PPV/CdTe complex leads to the maximum $J_{SC} = 0.305 \text{ mA} \cdot \text{cm}^{-2}$ and $V_{OC} = 0.60 \text{ V}$ which are attributed to the number of light harvesting layers and the thickness of complex. We should emphasize that our complex was fabricated in air with wet processes and its photoelectric characteristics were also measured in air. So the novel approach to fabricate this polymer/nanocrystals complex is promising to be applied to photovoltaic device, even solar cell fields.

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