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TiO_x Concentration Dependence of OPV Efficiency Optimization

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Abstract. Titanium oxide TiO_x material is used as electron transporter in organic photovoltaic cells (OPV). The layer was prepared between P3HT:PCBM as the active layer and the and aluminum electrode by spin coating technique. The synthesis and characterization of TiO_x is described. Using Raman spectroscopy technique TiO_x crystals show anatase structure. Varied concentrations of TiO_x and isopropanol solvent were performed. The most optimized device efficiencies up to 2,0% was achieved at a 1:20 ratio, which indicated more than 50% efficiency enhancement comparing with the device without TiO_x layer. The major improvement of the cell was originated from photocurrent enhancement.

Introduction

Organic photovoltaic (OPV) importantly provides opportunities to achieve cheap and flexible power conversion devices. The most promising configuration of photoactive material is bulk heterojunction which refers to blending between electron donor and electron acceptor. Electron donor is likely used conjugated polymer material such as poly (3-hexylthiophene) (P3HT) and poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV), while fullerene and its derivatives are likely used as electron acceptors such as Buckminsterfullerene (C_{60}) and 1-(3-methoxycarbonyl)propyl-1-phenyl [6,6]C_{61} (PCBM) [1]. Among various conjugated polymers and fullerenes, P3HT and PCBM are frequently selected to be used as photoactive layer for solar cell devices due to resulting high device efficiency [2,3]. OPV device mainly consists of indium-tin-oxide (ITO) coated glass serving as electrode, PEDOT:PSS serving as hole transportation, P3HT:PCBM serving as bulk heterojunction photoactive layer and an aluminum electrode. To improve the device efficiency, many approaches are carried out, but the most effective method is aimed to optimize the film morphology such as annealing [4-7]. A good quality of the film morphology leads to a better spectrum respond coverage and an increased electric conductivity [8]; however, the limitation of the device thickness prevents devices from fully absorbed optical electric field intensity because the light intensity near the aluminum electrode is low [9]. Titanium oxide (TiO_x) is the material of choice used as extra layer for electrical and optical performance enhancement due to their function as an optical spacer, hole blocking layer and electron transporting layer in the bulk heterojunction solar cells. Either solution based or sol gel based mixing with solvent (alcohol) is used as starting material. Therefore, the TiO_x layer could be easily prepared by spin coating technique. The highest record of device efficiency with such interlayer was found up to 5.0% [10]. The obvious effect of TiO_x layer is the enhancement of the photocurrent [9,10]; this indicates a good electron transportation behavior of the material. Additionally, many publications also indicate that the spectral responsivity of solar cell devices raise in the whole spectrum range comparing with devices without TiO_x layer [9,10]. The structure of the investigated devices consist of ITO coated glass substrate/PEDOT:PSS/P3HT:PCBM/ TiO_x/Al.

Experiment

Materials: Regioregular poly(3-hexylthiophene) was synthesized by the Grignard metathesis procedure according to McCullough [11]. PCBM was synthesized from the reaction of fullerene and methyl-4-benzoylbutyrate-*p*-tosyl-hydrazone, in close analogy to the method already described in the literature [12]. TiO_x precursor solution could be prepared by following procedure: Titanium (IV) isopropoxide (2.4 g, 8.44 mmol) was added dropwise using a syringe to 2-methoxyethanol (12.5 ml) in a two-neck flask at -4°C under an argon atmosphere. After reflux for 1h, the solution was cooled to -4°C and ethanolamine (1.27 g, 20.7 mmol) was added slowly. Then the mixture was refluxed again for 2h. After cooling to room temperature, the mixture was obtained as an orange solution. Subsequently, TiO_x precursor solutions were diluted with isopropanol to give various concentrations as shown in table 1.

Device fabrication: The solar cell devices were prepared according to the following procedure: The ITO coated substrates were patterning etched by 9M HCl for 10min; the scotch tape was used to mask the device area before dip-etch process. Consecutively, the substrates were cleaned with detergent and then ultrasonicated in DI water, acetone, chloroform and isopropanol for 15min in each step. After blow-drying with nitrogen, the substrates were performed with oxygen plasma cleaning for 5min. Highly conductive hole transporter obtained from poly(3,4-ethylenedioxylene-thiophene):polystyrene sulfonic acid (PEDOT:PSS Aldrich) was filtered through 0.45µm nylon filter and then spin coated on a cleaned ITO substrate at 2000 rpm. The PEDOT:PSS layer was annealed on hot plate at 120°C for 30min. Composite solution with P3HT and PCBM was prepared using 1,2-dichlorobenzene. The concentration was controlled in 2.0wt%. The active layer (P3HT:PCBM) was spin coated on PEDOT:PSS film at 1500rpm and then dried at 180°C for 20min. Afterwards, the TiO_x layer was prepared by spin coating from TiO_x precursor solutions at 8000 rpm. The wet film was hydrolyzed in air at room temperature for 30min and then heated at 150°C for 10min. Finally, the 200nm aluminum electrode was deposited on TiO_x layer. The effective area of the solar cell was restricted to $0.24 cm^2$.

Result and discussion

The surface morphology of P3HT:PCBM layer with and without TiO_x layer have been studied using atomic force microscope (AFM). Fig. 1a depicts the morphology of P3HT:PCBM layer. The film shows a phase separation texture with rough surface with a r.m.s. roughness of 3.08 nm. For the device with TiO_x covered layer, a rather smooth, uniform morphology with r.m.s. of ca. 0.89 nm is observed (Fig. 1b). The smooth layer observed as small grain features indicates a possibility of improved interface achievement between electrode and active layer. Furthermore, the TiO_x may also serves as protection for photoactive layer from aluminum thermal diffusion [13].

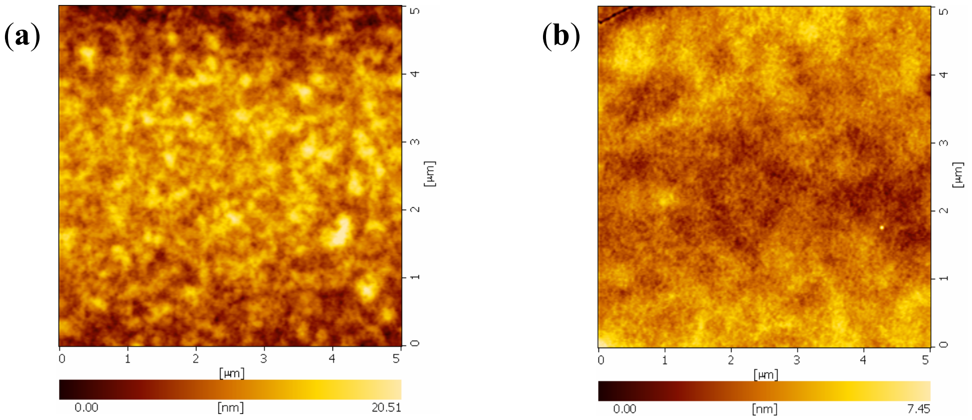
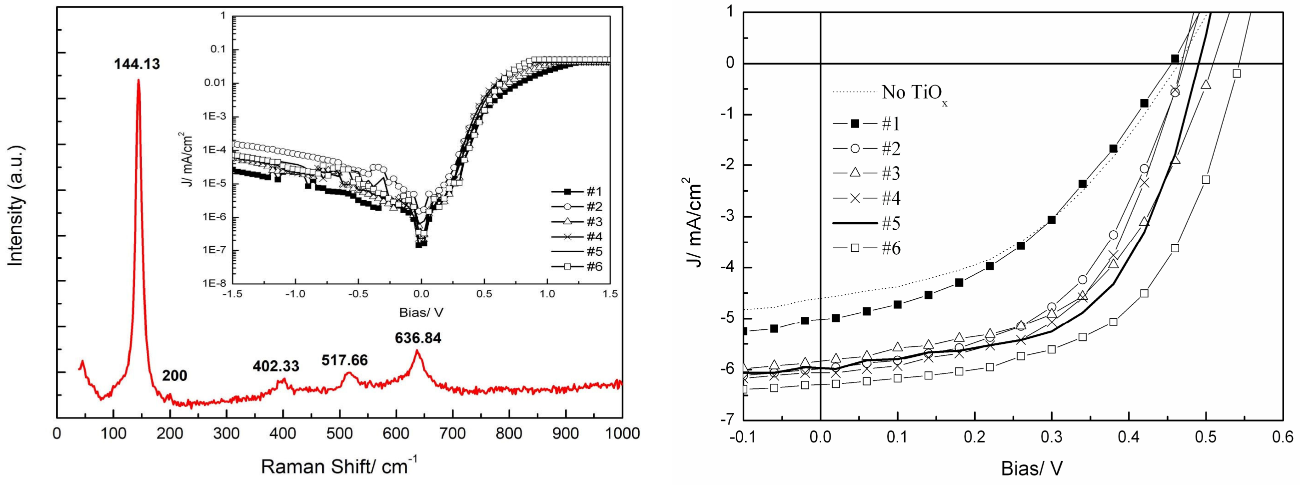


Figure 1. Surface morphology of fabricated devices; a) without TiO_x layer. b) with TiO_x layer.

The crystal structure study of TiO_x thin film was performed by Raman spectroscopy with 10 mw/cm^2 HeNe laser at 632.8 nm. Fig. 2a shows the Raman spectrum of the TiO_x film of diluted

TiO$_x$ precursor solution with isopropanol (1:2 by volume). The film was formed on glass slide substrate by spin coating at 2000 rpm. The wet film was left for 30min under air for hydrolysis and then baked on a hotplate at 150°C for 10 min; the process was repeated again to achieve dense structure resulting high Raman intensity. The signals indicate anatase single crystal phase; five peaks are noticed from the profile at 144.13, 200, 402.33, 517.66 and 636.84 cm^{-1} closely correlating to the 145, 197, 399, 519 and 639 cm^{-1} anatase single crystal Raman peaks of titanium dioxide [4].



(a) (b)

Figure 2. a) Raman spectra of TiO$_x$ thin film on glass substrate; the inset represents the dark current-voltage characteristics of the fabricated devices. b) Current-voltage characteristics of the investigated devices under illumination.

Table 1. Photovoltaic characteristics of the investigated bulk heterojunction devices.

Sample no.	TiOx:isopropanol (v/v)	V$_{oc}$ (V)	J$_{sc}$ (mA/cm^2)	Eff%	FF	R$_{sh}$ (Ω/cm^2)	R$_s$ (Ω/cm^2)
No TiO$_x$	-	0.46	4.61	0.92	0.43	376.26	33.2
#1	1:5	0.45	5.02	0.93	0.41	316.09	37.38
#2	1:8	0.47	5.97	1.44	0.52	555.37	20.46
#3	1:10	0.50	5.83	1.55	0.53	475.92	21.89
#4	1:13	0.46	6.05	1.56	0.56	628.04	13.59
#5	1:15	0.48	5.96	1.66	0.58	530.8	13.70
#6	1:20	0.52	6.16	1.92	0.60	541.06	18.18
#7	1:25	0.54	5.64	1.65	0.54	811.6	14.01

The investigated all organic photovoltaic cells possess the same configuration except the concentration of TiO$_x$ precursor solutions as shown in table 1. The photovoltaic performance of the devices was measured with Keithley 236 source measure unit under AM 1.5 sunlight with an energy density of 100 mW/cm^{-2} (solar simulator). The dark current of all devices indicate a good diode behavior as shown in the inset of Fig. 2a. The difference to the reverse currents may occur due to device thickness fluctuation. The effect of TiO$_x$ concentration indicates obvious result in illumination characteristics of the device; in Fig. 2b, the photocurrent is increased as the TiO$_x$ concentration is reduced. The solar cell device without TiO$_x$ layer exhibits 4.6 mA/cm^{-2} short-circuit current (J$_{sc}$), 0.46 V open-circuit voltage (V$_{oc}$) and 0.92% efficiency (n_e). In contrary, the device including 1:20 of TiO$_x$:isopropanal (v/v) shows an open-circuit voltage (V$_{oc}$) of 0.52V with J$_{sc}$ of 6.16mA/cm^{-2} and n_e up to 1.92%. The efficiency enhancement of the revised architecture device occur more than 50% improvement from original. Additionally, the electronic parameters such as series resistance and shunt resistance are greatly altered by effect of diluted TiO_x precursor solution as shown in table 1. However, with more diluted TiO_x precursor solution the device performance is dropped as shown in the final row of table 1.

Conclusion

The concentration dependence of TiO_x solution precursor leads to different thin film morphology which enhances the device efficiency. With lower TiO_x concentration, the surface morphology is smoother than with high concentration. The smooth surface results in better device ohmic contact as observed by low R_s. The photocurrent of the devices is enhanced as the TiO_x concentration is reduced, while the device V_{oc} is likely constant and reflects only the two electrode work functions difference; therefore, the efficiency of revised architecture device is increased.

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