



Effects of metal oxide as an anode interlayer for organic photovoltaics



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ABSTRACT

In this study, polymer:fullerene bulk-heterojunction hybrid solar cells with the structure indium tin oxide (ITO)/nickel oxide (NiO)/poly (3-hexylthiophene) (P3HT):[6, 6]-phenyl C61-butyric(PCBM):titania (TiO₂):platinum (Pt) nanoparticles (NPs)/Ca/Al were fabricated. The effects of a p-type NiO thin layer deposited by thermal evaporation between the active layer P3HT:PCBM:TiO₂:Pt and ITO on cell performance were examined. The results show that the NiO interfacial layer between the ITO and active layer can increase the efficiency and stability of the prepared hybrid solar cells. The optimum cell performance by ITO/NiO(5 nm)/P3HT:PCBM:TiO₂ (15 wt.%):Pt (0.03 wt.%)/Ca/Al (best cell structure) is an open-circuit voltage (Voc) = 0.61 V, short circuit current density (Jsc) = 6.22 mA/cm², fill factor (FF) = 54.8%, and η = 2.1%.

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1. Introduction

Polymer photovoltaic (PV) cells are a promising, renewable, and low-cost clean energy source [1,2]. They are becoming a viable alternative for large-scale energy production. Hybrid polymer/nanoparticle solar cells have a light-harvesting layer composed of semiconducting inorganic nanoparticles and a semiconducting conjugated polymer [3]. Hybrid polymer/nanoparticle solar cells have excellent potential to provide low-cost electricity, but have yet to achieve high-efficiency values. The key issues preventing solar cells from achieving commercially viable efficiencies reside within the colloid and interface science domain. Numerous reports have recently shown that certain metal oxides such as MoO₃ [4] and V₂O₅ [5] can improve device performance as anode buffer layers. The conventional device architecture for solar cells is based on glass/indium tin oxide (ITO)/poly (3,4-ethylene dioxothiophene):poly(styrene-sulfonate) (PEDOT:PSS)/poly (3-hexylthiophene) (P3HT):[6, 6]-phenyl C61-butyric(PCBM)/LiF/Al, and their power conversion efficiencies range between 4% and 5%. Moreover, recent studies have shown that PEDOT:PSS dispersions are highly acidic and corrosive to the ITO anode [6,7]. An alternative PEDOT:PSS requires the following characteristics: 1) sufficient optical transparency for allowing solar photon access to the active layer, which requires wide band-gap semiconductors ($E_{\text{gap}} > 3$ eV) that are transparent in the visible spectral region; 2) greater than the efficient transmission of the hole, and prevent the transfer of electrons;

and 3) an improved ambient chemical stability [8–10]. Nickel oxide (NiOx) is a well-known p-type transparent conducting oxide that exhibits a higher work function; thus, it is more favorable for hole injection into organic materials [11].

In this study, polymer:fullerene bulk-heterojunction hybrid solar cells with the structure ITO/nickel oxide (NiO)/P3HT:PCBM: titania (TiO₂):platinum (Pt) nanoparticles (NPs)/Ca/Al were fabricated. The p-type NiO thin layer was deposited by thermal evaporation between the active layer P3HT:PCBM:TiO₂:Pt and ITO anode. The conventional hole transport layer PEDOT:PSS was replaced by a 5 nm thick NiO layer in this study. Moreover, the effects of the NiO layer, and TiO₂ and Pt content in the active layer on cell performance were examined.

2. Experimental details

2.1. Materials

The regioregular P3HT (Aldrich, 99.995%) and PCBM-61 (Rieke Metals, Inc.) were used as the p-type semiconducting polymer and n-type semiconductor, respectively. Chlorobenzene (Aldrich, 99.8%) and Chloroplatinic acid (H₂PtCl₆·6H₂O, SHOWA) were used as purchased to synthesize Pt colloids. For typical reactions, H₂PtCl₆·6H₂O was dissolved in ethylene glycol (SHOWA, 99.5%).

2.2. Preparation of TiO₂ and Pt colloids

Pt colloids were prepared using the polyol method. For typical syntheses, 5 mL of ethylene glycol was added into 10 mL of water, followed by the addition of 0.1 g H₂PtCl₆ and reflux at 80 °C with vigorous stirring for 4 h. Thereafter, the solution was placed into the

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rotary evaporator, and the Pt was recovered from its H₂O fraction. Conversely, TiO₂ colloids were prepared from tetrabutyl orthotitanate, hydrochloric acid, and n-butanol by using the sol–gel procedure. The detailed description is provided in our previous study [12].

2.3. Preparation of Al/Ca/P3HT:PCBM:TiO₂:Pt/NiO/ITO hybrid solar cell

The hybrid solar cell devices were fabricated using the spin-coating process. All films were deposited onto commercially patterned ITO substrates (approximately 10 Ω/sq, thin-film devices) after 5 min of ultrasonic cleaning in acetone followed by isopropyl alcohol. Substrates were O₂ plasma-cleaned immediately prior to hole transport layer deposition (HTL) deposition in 106.6 Pa. The HTL was deposited by thermal evaporation of NiO with 5 nm thickness in sequence under a high vacuum (5×10^{-6} Pa). An active film composed of P3HT and PCBM ratio 1:1 dissolved in chlorobenzene and stirred for 12 h was prepared. A desired amount of TiO₂ and Pt colloids was added into the P3HT:PCBM solution and stirred for 12 h. The product was labeled PCTPtX (X is a number that represents the wt.% of Pt). Thereafter, the active layer was prepared by spin-coating at 1000 rpm on the NiO layer and annealing at 150 °C for 20 min. The cathode was produced by thermally depositing a 60-nm-thick Ca layer and a subsequent 80-nm-thick aluminum layer in a vacuum of 1.33×10^{-4} Pa. The area of the device was typically 0.2 cm².

2.4. Characterization

The AFM (Veeco DI3100) was used to probe the surface morphology of the coated films with a monolithic silicon probe under tapping mode. The tip of the probe is shaped like a polygon based pyramid with a height of 10–15 μm. The baseline noise was less than 0.1 nm. The photoluminescence (PL) spectra were obtained using a Horiba Jobin Yvon Fluoromax-4 Spectrofluorometer with a 450 nm excitation wavelength. The UV–vis absorption spectrum was recorded using a Jasco Model V-650 UV–vis–NIR spectrophotometer. The performance of the photovoltaic cells was measured using a calibrated AM1.5G solar simulator (Oriol 300 W) at 100 mW/cm² light intensity adjusted with a standard PV reference cell (monocrystalline silicon solar cell, calibrated at NREL, CO, USA). The current–voltage (J–V) characteristics were measured with a source meter (Keithley 2400) and an AM1.5 solar simulator (MFS-PV-Basic) was employed as the light source. All fabrication steps and characterizations were performed in a controlled atmosphere. The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of 71 nm. The incident photon-to-current conversion efficiency (IPCE) spectra were recorded by illuminating the samples with a 300 W Xenon lamp, dispersed using a Dongwoo-optron (South Korea) DM151i single-grating monochromator. The hybrid photovoltaic cell properties were compared with a pristine P3HT:PCBM system, and the effects of TiO₂ addition on the performance of hybrid photovoltaic cells were examined. The crystalline structure of the active layer was analyzed using X-ray powder diffraction data were collected at room temperature on the X-ray diffractometer (XRD) (PANalytical X'PerPRO MPD) using Cu Kα radiation, $\lambda = 1.54056$ Å between 20° and 60° (2θ). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under a nitrogen flow using a DuPont Model 951 thermogravimetric analyzer and DuPont Model 910S differential scanning calorimeter at a heating rate of 20 °C/min and 10 °C/min, respectively. The TGA and DSC samples were prepared by spin-coating the precursor solution on a glass substrate, followed by curing at various temperature steps, as described in the film preparation. Impedance spectroscopy was measured using an impedance analyzer (CHI6143D) with an AC signal of 0.5 V in the 0.05 Hz–100 MHz frequency range.

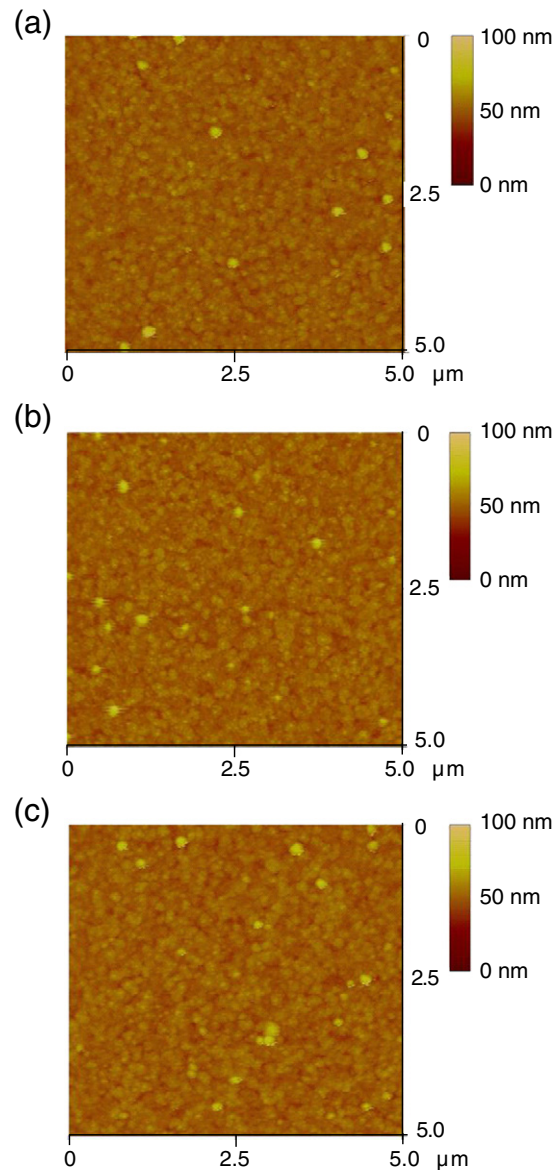


Fig. 1. AFM images of NiO deposited on ITO substrate with different thickness: (a) 5 nm, (b) 10 nm, and (c) 20 nm.

3. Results and discussion

Fig. 1 shows the AFM images of the NiO layers of 5, 10, and 20 nm thickness deposited on the ITO substrate (NiO/ITO films). The average

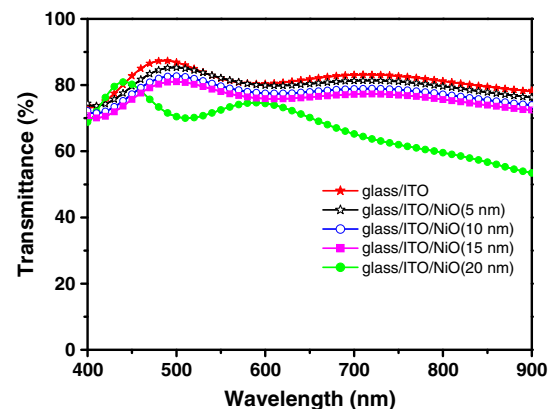


Fig. 2. UV–vis spectra of NiO deposited on the ITO substrate with different NiO thickness.

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