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Ligand chemistry of titania precursor affects transient photovoltaic behavior in inverted organic solar cells

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The chemistry of the precursor from which charge transport layers are formed can significantly affect the device performance of organic solar cells. Here, we compare two common precursors that are used to generate titania electron transport layers and elucidate their effects on the transient characteristics of inverted bulk-heterojunction polymer solar cells comprising poly(3-hexyl thiophene) and [6,6]-phenyl-C₆₁-butyric acid methyl ester. Substituting the isopropyl ligands of titanium isopropoxide with 2-methoxyethanol leads to electron transport layers that require a shorter illumination time to fill shallow electron traps. Furthermore, organic solar cells with titania electron transport layers prepared with such pre-modified titania precursor exhibit higher power-conversion efficiencies stemming from lower trap densities. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4795287>]

As an alternative to inorganic solar cells, organic solar cells promise to be low cost, light weight, and possessing processing flexibility. To date, organic solar cells have achieved power-conversion efficiencies over 10%.^{1–3} The initial progress of organic solar cells was based on the development of photoactive layer architecture.^{4–6} Specifically, the shift from single-junction to heterojunction active layers has resulted in substantial improvements in the fill factor and power-conversion efficiency of devices. Single-junction architectures adopt one organic semiconductor as photoactive layer in which the work function difference of electrodes and Schottky-type potential barrier at the metal/organic contacts are responsible for dissociating excitons to generate free electrons and holes.⁴ Hetero-junction architectures introduce two organic semiconductors to the photoactive layer in which the built-in potential between the two organic semiconductors easily dissociates excitons to generate free charges.⁵ Subsequently, bulk-heterojunction photoactive layers comprising mixtures of electron donor and electron acceptor have been shown to exhibit yet higher efficiencies given the increase in interfacial area between the electron donor and electron acceptor.⁶

A strategy to further improve the device characteristics of organic solar cells involves the introduction of charge transport and blocking layers at the carrier collecting interfaces. For example, hole transport layers, such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), PEDOT:PSS, vanadium oxide, and molybdenum oxide,^{7,8} have been introduced to the hole-collecting interface in organic solar cells; these layers substantially improve hole extraction at the anode and retard electron transport. The result of the incorporation of these blocking layers is an enhancement in the

fill factor and power-conversion efficiency of devices. To further improve charge transport efficiency in organic solar cells, electron transport layers, such as titania and zinc oxide,⁹ have been introduced at the electron-collecting interface to increase charge selectivity to the cathode.

Although solution-processed charge transport layers provide charge selectivity at the active layer-electrode interfaces in organic solar cells, trap sites in these charge transport layers act as recombination centers,^{10–12} effectively decreasing short-circuit current densities and fill factors of devices. We have previously reported the presence of electron trap sites in solution-processed titania layers; these trap sites can be filled under illumination, resulting in transient improvements of photovoltaic characteristics.¹³ The ability to prepare charge transport layers with low trap densities is therefore critical for further improvement in devices. Here, we compare two different precursors that are commonly used to create titania electron transport layers, titanium isopropoxide^{13–15} (hereafter known as precursor **1**) and a titanium precursor that is obtained after **1** undergoes ligand exchange with 2-methoxyethanol (hereafter known as precursor **2**),^{9,16,17} and we elucidate their influence on device performance of inverted organic solar cells. The alteration of ligand chemistry has allowed us to access an electron transport layer that exhibits faster transient characteristics and higher photoconductivity in organic solar cells.

We prepared titania electron transport layers with precursors **1** and **2** via sol-gel condensation and then fabricated organic solar cells atop these electron transport layers in the inverted configuration per Fig. 1. Precursor **1** was purchased from Sigma Aldrich and diluted with isopropyl alcohol to form a 1 wt. % solution. To prepare **2**, we exchanged the isopropyl groups of **1** using a previously published procedures.¹⁷ Briefly, **1** (5 ml), 2-methoxyethanol (CH₃OCH₂CH₂OH, 20 ml) and ethanolamine (H₂NCH₂CH₂OH, 2 ml) were sequentially injected into a three-neck flask equipped with a water condenser and nitrogen line. After stirring at room temperature, 80 °C, and then 120 °C for 1 h each, successful

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ligand exchange was indicated by a color change from clear to a burgundy hue.¹⁷ Precursor **2** was then used after it was diluted in methanol to a 1:200 volume ratio to yield an approximately 0.7 wt. % solution.

With the two titania precursors in hand, we fabricated inverted bulk-heterojunction polymer solar cells comprising poly(3-hexylthiophene), P3HT, and [6,6]-phenyl-C₆₁-butyric acid methyl ester, PCBM (Fig. 1). After cleaning the pre-patterned ITO on glass substrates (15 Ω/sq.; Colorado Concept Coatings) by sonication in acetone and isopropyl alcohol, 40-nm thick titania electron transport layers were formed on these substrates by depositing and hydrolyzing isopropyl alcohol-diluted **1** or methanol-diluted **2** according to published procedures.^{9,13–17} To form the photoactive layer, P3HT (Merck Chemical Ltd.) and PCBM (American Dye Source, Inc.) were co-dissolved at a 1:1 mass ratio in a 2.4 wt. % solution in chlorobenzene. This solution was directly spin-coated on the two different titania layers atop ITO substrates at 500 rpm for 60 s, resulting in 180-nm thick photoactive layers. After thermal annealing at 170 °C for 1 min, 100-nm thick gold was evaporated through stencil masks to complete the inverted solar cells having an active area of 0.18 cm². Current density-voltage (J-V) characteristics were acquired using a Keithley 2400 source measurement unit under AM 1.5G 100 mW/cm² illumination in air.

To examine the thin-film properties of the two titania layers, we constructed metal-oxide-semiconductor (MOS) capacitors on p-type Si wafer (Boron-doped; 1–20 Ω·cm). The wafers were first subjected to sequential sonication in acetone and isopropyl alcohol, followed by rinsing in water and exposure to UV/ozone to descum the surface. Then, solutions of **1** and **2** were spin-coated on Si substrates and hydrolyzed following procedures analogous to those used to form the electron transport layers for inverted organic solar cells. Evaporation of 100-nm thick gold through stencil masks completed the fabrication of MOS capacitors, defining an active area of 0.1 cm². C-V characteristics were acquired at 100 kHz using ModuLab 2101A (Solartron Analytical) in the dark in air to quantify the trap densities of the titania layers given that these traps substantially affect device characteristics of organic solar cells.^{10–13}

Figures 2(a) and 2(b) show the J-V characteristics of P3HT:PCBM inverted organic solar cells with titania electron transport layers prepared with precursors **1** and **2**,

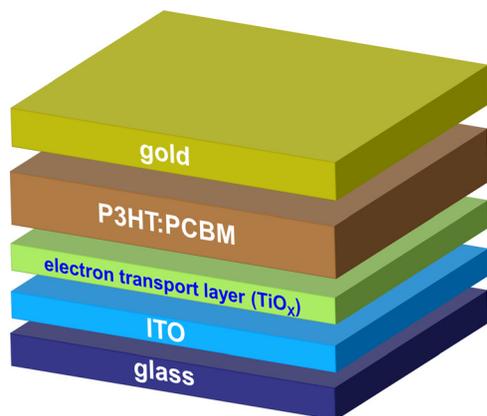


FIG. 1. Schematic illustration of a P3HT:PCBM organic solar cell constructed in the inverted configuration.

respectively. The J-V characteristics of a representative device with titania layer prepared with **1**, shown in Fig. 2(a), exhibit an initial open-circuit voltage, V_{OC} , of 0.31 V and a short-circuit current density, J_{SC} , of 2.6 mA/cm² under illumination. With increasing illumination time, however, we observe that its V_{OC} , J_{SC} , and fill factor all improve. As we previously reported,¹³ such transient characteristics stem from the presence of electron traps in the titania electron transport layer, which in turn decreases its photoconductivity. On extended illumination of the photoactive layer, photogenerated electrons fill these shallow trap sites, resulting in a gradual increase in the photoconductivity. Accordingly, the device characteristics, including V_{OC} , J_{SC} , fill factor, and power-conversion efficiency, gradually increase. Upon saturation, the device exhibits $V_{oc}=0.53$ V and $J_{sc}=7.2$ mA/cm². While this improvement in device V_{OC} and J_{SC} occurs in less than 3 min, it is only after further illumination (5 min) that the fill factor improves and saturates at 0.56.

Compared to the characteristics exhibited by devices with **1** as the titania layer, devices with **2** as the titania layer are quantitatively different. While the fill factor remains poor, the initial V_{OC} and J_{SC} of a representative device having titania layer prepared by **2** are substantially higher. Specifically, we observe in Fig. 2(b) an initial V_{OC} of 0.53 V and a J_{SC} of 7.9 mA/cm²; these values are comparable to the final values obtained when the device characteristics saturate on extended illumination. While the fill factor takes longer to saturate compared to the other device characteristics, its saturation time (1 min) is substantially shorter than that observed in the device having **1** as its titania layer. Given that such transient photovoltaic behavior results from trap sites in the titania layer,¹³ this shorter saturation time implies less traps in the titania layer of **2** compared to that of **1**.

To compare the transient photovoltaic behavior of P3HT:PCBM inverted organic solar cells with the two different titania electron transport layers, we summarized the J_{SC} and power-conversion efficiency as a function of illumination time in Figs. 2(c) and 2(d), respectively. While the J_{SC} of device with titania layer **1** took about 3 min to saturate, we observe in Fig. 2(c) that the J_{sc} of the device with titania layer **2** has practically saturated from the initial measurement. This difference translates to yet larger differences in the transient characteristics of the device efficiency, as shown in Fig. 2(d). The efficiency of the device with titania layer **1** saturates after 5 min illumination, whereas that of the device with titania layer **2** saturates after 1 min. Interestingly, the device with titania layer **2** also exhibits higher J_{sc} and, accordingly, efficiency upon saturation. We attribute this higher J_{SC} to higher photoconductivity of titania layer **2**, facilitating more efficient electron extraction at the cathode.

To quantitatively compare the trap densities, which can ultimately affect device performance of organic solar cells,^{10–13} in the titania layers derived from **1** and **2**, we fabricated MOS capacitors with titania layers on p-type Si wafer and measured their C-V characteristics in the dark. We believe that the trap density extracted from MOS capacitors is a good proxy for the trap density of titania in organic solar cells because bulk—as opposed to interfacial—traps dominate the characteristics of titania. Given the presence of trap sites in the titania layer, we expected to see hysteresis in the

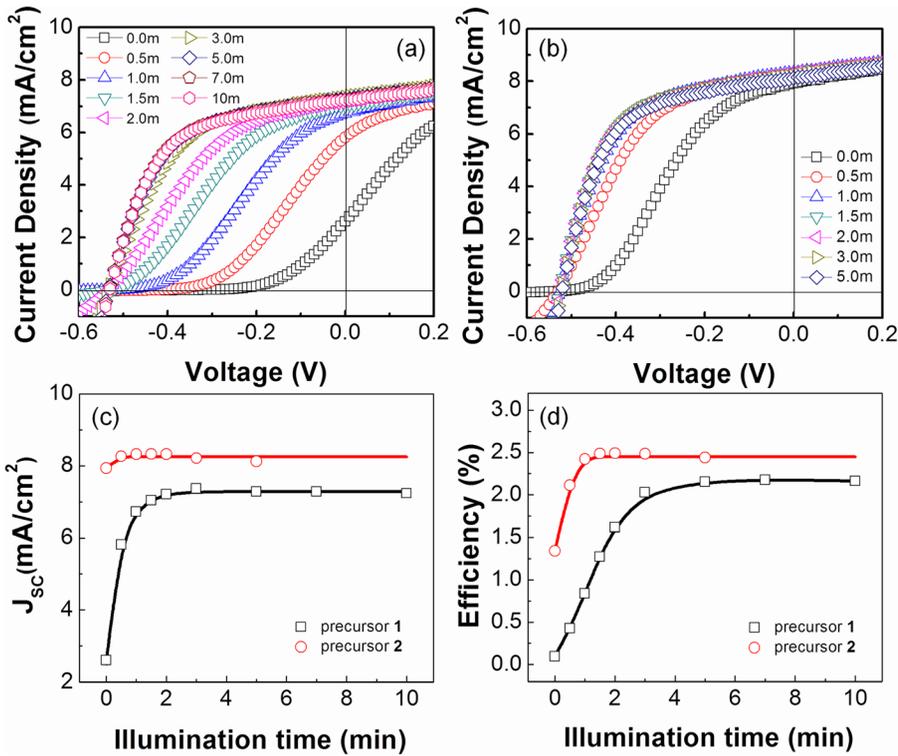


FIG. 2. J-V characteristics under illumination of P3HT:PCBM inverted solar cells with two different titania electron transport layers, prepared with (a) **1** or (b) **2**. The evolution of (c) extracted short-circuit current density and (d) efficiency is also plotted to contrast the transient photovoltaic behavior of organic solar cells having titania layers prepared from the different precursors.

C-V characteristics whose magnitude will depend on the extent of traps present. Quantification of the midgap voltage shift (ΔV_{mg}) then allows estimation of trap density.¹⁸ Figure 3 show the C-V characteristics of two representative capacitors, one with an oxide layer derived with **1** and the other with **2**. Given that our MOS capacitors were constructed on p-type Si wafer, the application of a negative voltage on the metal gate should induce an accumulation of holes in Si. But when a positive bias is instead applied to the metal gate electrode, holes are extracted from Si, resulting in depletion states and inversion beyond the threshold voltage. This accumulation and depletion of holes when negative and positive biases are applied, respectively, result in the inverse S-shaped curve in the C-V characteristics shown in Fig. 3. While the C-V curves from the two MOS capacitors are characteristically similar, they exhibit different extents of hysteresis. Specifically, the capacitor with titania layer prepared using **1** is more hysteretic compared to that of the capacitor using precursor **2**. Consistent with the transient photovoltaic data shown in Fig. 2, the data plotted in Fig. 3 indicate that the titania that is generated from **2** has a lower trap density. We extracted ΔV_{mg} from the C-V characteristics from which trap density, ΔN_{ot} can be calculated using the following equation:¹⁸

$$\Delta N_{ot} = -\frac{C_{ox}\Delta V_{mg}}{qA}$$

where C_{ox} is the capacitance of titania under accumulation, q is the electron charge, and A is the area. ΔV_{mg} is defined as the voltage difference at the average capacitance under accumulation and depletion modes, as indicated in Fig. 3. From Fig. 3(a), we estimate ΔV_{mg} for the titania layer prepared with **1** to be 56 mV, resulting in a trap density of $1.7 \times 10^{10}/\text{cm}^2$ in the dark. The ΔV_{mg} for the capacitor generated with titania from **2** is instead 25 mV, or less than half that of the titania generated with **1**, resulting in a trap density of $0.7 \times 10^{10}/\text{cm}^2$ in the dark. Our calculations thus indicate that the trap density in titania **1** is more than 2.5 times higher than that in titania **2**. We speculate that this discrepancy originates from differences in the precursors' hydrolysis rates. Specifically, it is well-known that **1** undergoes hydrolysis quickly, which often results in incomplete reaction.^{19–21} Accordingly, the presence of dangling bonds, residual OH groups, and oxygen vacancies in the titania results in poor charge transport properties.^{19–21} Changing the ligand chemistry of the titania precursor has been shown to slow down hydrolysis and to induce a more efficacious

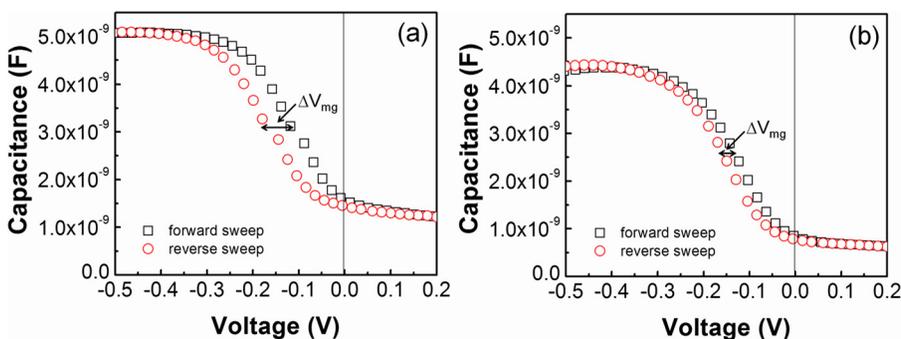


FIG. 3. C-V characteristics of MOS capacitors with two different titania layers, prepared with (a) **1** and (b) **2**. The extent of hysteresis in the C-V characteristics is proportional to the trap densities in these titania layers.

reaction.²⁰ Our device characterization herein suggests that titania precursors **2** undergoes slower hydrolysis and forms better titania layers for solar cells given their lower trap densities and higher photoconductivities. Ideally, one can also change the reaction conditions (temperature, time, etc.) to increase the extent of hydrolysis. In fact, controlling the humidity during hydrolysis has been shown to alter reaction rates.²¹ But controlling the extent of hydrolysis in this manner is challenging in practice given that the onset of reaction occurs early in the spin-coating process.²⁰

In conclusion, we demonstrated that the chemistries of titania precursors can significantly affect the thin-film properties of the resulting electron transport layers, ultimately affecting the device performance of organic solar cells. Specifically, by first carrying out ligand exchange of commercially available titanium isopropoxide with 2-methoxyethanol prior to its hydrolysis to titania, we can generate electron transport layers with 40% of the trap density in the electron transport layers that are directly converted with titania isopropoxide. This decrease in trap density results in devices with shorter saturation time and higher performance. When it comes to such sol-gel chemistries for generating charge transport layers, our study indicates that the proper selection of metal oxide precursors is critical for achieving solution-processed organic solar cells with high performance.

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