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## Stoichiometric dependence of $\text{TiO}_x$ as a cathode modifier on band alignment of polymer solar cells



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### ABSTRACT

In this study, we systematically investigated the stoichiometric dependence of titanium oxide ( $\text{TiO}_x$ ,  $x=1.56\text{--}1.93$ ) as a cathode modifier on the device performance of polymer solar cells. Electronic structures of the synthesized  $\text{TiO}_x$  modifier layers were controlled by tuning the compositions of various O/Ti ratios. The effective cathode work-functions and the corresponding device performances of polymer solar cells are systematically changed as a result of inserting the  $\text{TiO}_x$  modification layers. Interfacial modification of the Al cathode with a low O/Ti ratio of  $\text{TiO}_x$  layer yields the best performing photovoltaic device as a result of a largest built-in potential. The correlation of power conversion efficiencies and carrier dynamics of these devices by inserting various  $\text{TiO}_x$  modification layer is further examined by using the Mott-Schottky analysis and the impedance spectroscopy technique. The consistent result shows an enhanced carrier collection efficiency and a reduced charge recombination rate of the device via adequate band alignment between the photoactive layer and the cathode using the  $\text{TiO}_x$  modification layer with an optimized O/Ti ratio.

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### 1. Introduction

Polymer photovoltaics have attracted substantial research interest in offering a cost-effective approach of converting solar energy into electricity compared to conventional inorganic counterparts such as Si or GaAs [1–6], benefiting from the possibility of solution processing, patterning, and roll-to-roll manufacturing. Substantial progress has been made in improving the photo-to-electron conversion efficiency of polymer photovoltaics, both in academic and industrial studies in the last decade [7–10]. Recent advances have involved achieving high photovoltaic efficiencies over 10% to incorporate new small band gap semiconducting polymers [11], which are close to the requirement for entering the business market. Because of the short diffusion length of excitons in a semiconducting polymer (less than 20 nm) [12], a polymer solar cell with high photocurrent quantum efficiency typically requires exciton generation that is close to the donor–acceptor interface. The most commonly used device structure is the bulk heterojunction (BHJ) solar cell, which consists of an intimate donor–acceptor interpenetration morphology in the photoactive layers for creating a large interface, resulting in a high

quantum yield of exciton dissociation, and these phase-separated domains should be optimized to ensure efficient dissociations of photogenerated excitons and continuous pathways for transporting charge carriers to electrodes [13,14]. The device performances of polymer solar cells have been largely improved by optimizing the photoactive materials such as conjugated polymer donor and organic or inorganic acceptors [15]. Another important issue to improve the device performance in a polymer solar cell is related to the deposition of a functional interlayer which may enhance the carrier collection or reduce the charge recombination via adequate band alignment between the photoactive layer and electrode. Accordingly, many functional interlayers have been reported to enhance carrier collection efficiencies in polymer solar cells. For hole collection and transportation, PEDOT:PSS [16] and other metal oxide such as  $\text{MoO}_3$  [17],  $\text{V}_2\text{O}_5$  [18] and graphene oxide [19] had been widely used, whereas  $\text{Cs}_2\text{CO}_3$  [20],  $\text{ZnO}$  [21] and  $\text{TiO}_x$  [22] are used as electron transport layers. Among the mentioned electron transporting materials, thin films  $\text{TiO}_x$  are of great interest because they are solution processable, transparent and highly air stable. The thin films  $\text{TiO}_x$  have been demonstrated to act as an optical spacer, [23] a hole blocking layer [24] or an electron transport layer [25] to improve the polymer photovoltaic efficiencies. In addition, the thin layer of  $\text{TiO}_x$  can act as active scavenging layer for removing  $\text{O}_2$  and  $\text{H}_2\text{O}$  from the semiconducting polymer,

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which may extend the lifetime of polymer photovoltaic devices and field-effect transistors (FETs) [26].

Although the unique advantages of using  $\text{TiO}_x$  as a cathode modifier to improve the power conversion efficiency of a polymer solar cell had been demonstrated by various reports, the dependence of stoichiometric O/Ti ratios of  $\text{TiO}_x$  thin layers on the device performance is still lacking. In this work, we would like to demonstrate the systematic investigation on the stoichiometric dependence of  $\text{TiO}_x$  thin films, ( $x=1.56\text{--}1.93$ ) as cathode modifiers on the device performances of polymer solar cells by tuning the electronic structures of the synthesized  $\text{TiO}_x$ . The interplay of power conversion efficiencies, interfacial band alignments and carrier dynamics of these devices by inserting  $\text{TiO}_x$  modifier layers with various O/Ti ratios were further examined by using Mott–Schottky analysis and the impedance spectroscopy technique.

## 2. Materials and Characterizations

The amorphous  $\text{TiO}_x$  were synthesized according to literature with some modification to control the stoichiometric ratios and electronic structures of  $\text{TiO}_x$  [24]. In brief, 2-methoxyethanol ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ , Acros, 99+%) and ethanolamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ , Acros, 99%) were first mixed in a three-necked flask, and titanium (IV) isopropoxide ( $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , Acros, 98+%) was then injected after 10 min stirring. The mixture was kept at 80 °C for 1 h for alcoholysis reaction, and then raised to 120 °C to enhance condensation reaction. [27,28] The heating durations at 120 °C lasted for 3, 6 and 9 h to obtain  $\text{TiO}_x$  with different O/Ti ratios.

For materials characterization, the  $\text{TiO}_x$  morphologies were imaged by using a FEI Tecnai G20 transmission electron microscope (TEM) which operated at 200 kV. XPS spectra were obtained with a VG Scientific ESCALAB 250 system, where the X-ray source was generated from the Al target (1486.8 eV) with the pass energy of 20 eV. Mott–Schottky and impedance spectroscopy measurements were carried out by using a potentiostat instrument with impedance modules (Metrohm Autolab). The typical Mott–Schottky measurement was operated at a frequency of 3000 Hz. Impedance spectroscopy measurements were performed under A.M. 1.5 illumination at the open-circuit voltage conditions with AC electrical frequencies ranging from 1 MHz to 20 Hz and oscillating amplitudes below 10 mV (rms) to maintain linearity response. For device fabrication, a 50-nm thick layer of PEDOT:PSS (Baytron P 4083) was first spun-cast onto the ITO electrode and baked at 150 °C for 10 min in air. The photoactive layer was deposited on top of the PEDOT:PSS layer by spin coating using a 1:0.8 weight ratio blend of P3HT:PCBM dissolved in chlorobenzene.

The photoactive layer was approximately 100 nm thick. The 1-butanol diluted  $\text{TiO}_x$  thin films with various O/Ti ratios were thus spin-coated on the photoactive layers, followed by a heating treatment under ambient atmosphere at 80 °C for 10 min. The thickness of  $\text{TiO}_x$  thin films are about 20 nm. Aluminum electrodes (100 nm) were thermally evaporated onto the photoactive layers at a vacuum pressure of  $5 \times 10^{-6}$  Torr. All devices were annealed at 150 °C for 10 min inside the glove box before measurements.

## 3. Results and discussion

Fig. 1(a)–(c) demonstrates the TEM images of the as-synthesized  $\text{TiO}_x$  with different reaction times of 3, 6 and 9 h. A tendency of increased average particle sizes with prolonged reaction durations was observed. Fig. 2(a) and (b) shows the representative XPS spectra of Ti 2p and O 1s peaks of  $\text{TiO}_x$  synthesized with various reaction durations. For comparison, the XPS spectra of Ti 2p and O 1s peaks of the crystalline  $\text{TiO}_2$  (after calcination of  $\text{TiO}_x$  at 450 °C) is also presented, which shows a typical signature of the  $\text{TiO}_2$  anatase phase. (See Supporting information of XRD spectra in Fig. S1.) As shown in Ti 2p core level spectra in Fig. 2(a), the binding energies of two main peaks located at 458.8 eV ( $\text{Ti } 2p_{1/2}$ ) and 464.3 eV ( $\text{Ti } 2p_{3/2}$ ) correspond to  $\text{Ti}^{4+}$  bonding are observed in all the  $\text{TiO}_x$  samples with various reaction durations. The same peak positions of the Ti 2p core level spectra are also found in the crystalline anatase  $\text{TiO}_2$  sample. However, un-symmetric shaped and broadened Ti 2p spectra of all  $\text{TiO}_x$  samples are observed compared to those in the crystalline  $\text{TiO}_2$  sample, revealing the existence of defects in the as-synthesized  $\text{TiO}_x$  samples [29,30]. The de-convoluted components centered at 456.8 eV in all the  $\text{TiO}_x$  samples are ascribed to the  $\text{Ti}^{3+}$  species as a result of presence of defects, which are commonly observed in amorphous titanium oxide from sol–gel reaction [31,32]. The presence of defects in all the  $\text{TiO}_x$  samples can be further evidenced from the O 1s spectra as shown in Fig. 2(b), where two oxygen-containing components of  $\text{Ti}^{4+}\text{--O}$  bonding (530.1 eV) and oxygen-deficient (531.6 eV) peaks were resolved. The quantitative determination of compositions of different  $\text{TiO}_x$  samples were performed by integrating the areas under the de-convoluted peaks in Ti 2p and O1s spectra, where the sensitivity factors of 0.711 for O and 1.798 for Ti were also taken into account during calculations. The O/Ti ratios for these three samples with reaction durations of 3, 6 and 9 h are found to be 1.56 (low), 1.76 (medium) and 1.93 (high), respectively indicating different inherent oxygen deficiencies in  $\text{TiO}_x$  with various reaction durations. The amorphous signatures of these synthesized  $\text{TiO}_x$  samples were further confirmed by wide angle X-ray diffraction spectra as

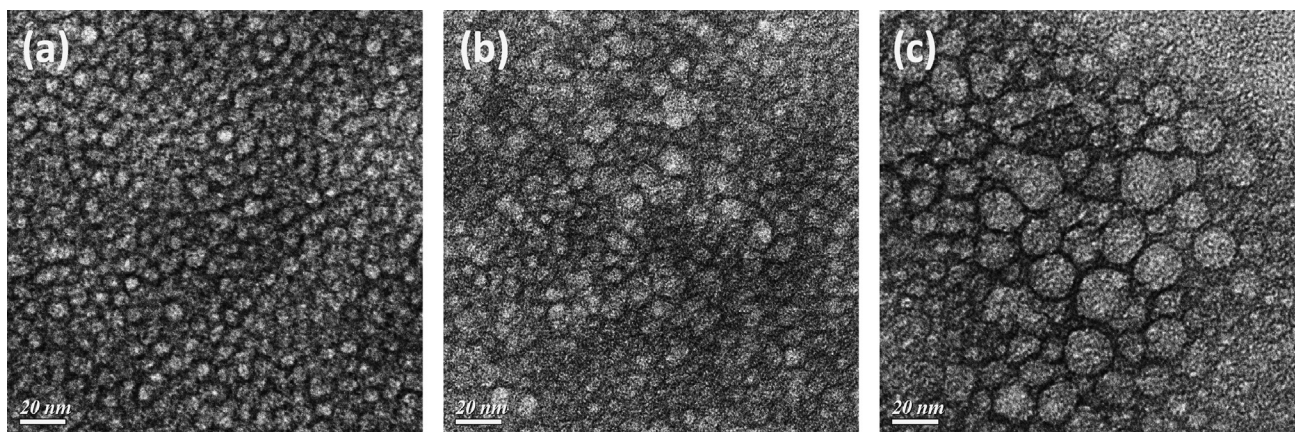


Fig. 1. TEM images of  $\text{TiO}_x$  with different reaction durations at 120 °C (a) 3 (b) 6 (c) 9 h.

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