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The appearance of Ti^{3+} states in solution-processed TiO_x buffer layers in inverted organic photovoltaics

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We study the low-temperature solution processed TiO_x films and device structures using core level and valence X-ray photoelectron spectroscopy (XPS) and electronic structure calculations. We are able to correlate the fraction of Ti^{3+} present as obtained from Ti 2p core level XPS with the intensity of the defect states that appear within the band gap as observed with our valence XPS. Constructing an operating inverted organic photovoltaic (OPV) using the TiO_x film as an electron selective contact may increase the fraction of Ti^{3+} present. We provide evidence that the number of charge carriers in TiO_x can be significantly varied and this might influence the performance of inverted OPVs. *Published by AIP Publishing.*
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Metal oxides are of increasing interest as materials for opto-electronic devices, and have been extensively used as functional layers in organic photovoltaics (OPVs). Among these metal oxides, solution processed titanium oxide (TiO_x) is of particular interest as an electron acceptor/collector due to its low cost, facile synthesis, long-term stability, and a conduction band minima that is low enough in energy to accept/collect electrons from most organic semiconductors.[1,2]

Currently, the most popular use of TiO_x is as an electron selective contact in an inverted OPV architecture.[2] An inverted OPV has the cathode on the bottom and the anode on the top, and requires highly transparent and conductive materials for efficient operation—a role that can be fulfilled with TiO_x.[3] There are, however, open questions relevant to device performance, and related to the functionality of the TiO_x layer, that stem from uncertainties in the chemical composition and electronic structure of TiO_x. In this letter we study an inverted OPV device structure with a TiO_x electron selective contact using core level and valence X-ray photoelectron spectroscopy (XPS). There have been previous core level XPS[4–6] and computational[7] studies on the electronic structures of TiO_x. A combined core level and valence XPS study is of particular value as the valence spectra can be directly compared with electronic structure calculations, allowing the relationship between core level features and valence electronic structure to be explored. Previous experimental studies of the valence band in TiO_2 have focused on isolated defects on otherwise pristine surfaces of single crystal;[8] herein, we focus on an actual solution processed inverted OPV TiO_x buffer layer prepared by the sol–gel method.

The differences in the electronic structure between stoichiometric TiO_2 and TiO_x seem to be primarily due to oxygen vacancies,[7] although excess interstitial Ti has also been suggested.[8] The most noticeable differences are the presence of Ti^{3+},[5] and the appearance of occupied states within the band gap.[8] OPVs with TiO_x have been reported with Ti^{3+} fractions ranging from near 0% (undetectable Ti^{3+} content) to 27%.[6,9–11] A previous study using nanocrystalline TiO_x in dye-sensitized solar cells (DSSCs) found that as the Ti^{3+} fraction increased, the device performance *decreased*.[12] However, no such correlation seems to exist in OPVs using TiO_x as an electron extraction layer. The wide range of Ti^{3+} content in these TiO_x films, and the lack of correlation between the Ti^{3+} content and the device performance highlights the need to understand the role of Ti^{3+} on the electronic structure of solution processed TiO_x films used as electron selective contacts in inverted OPVs.

TiO_x films were prepared by doctor blading an ITO substrate with gel of titanium butoxide ($C_{16}H_{36}O_4Ti$) dissolved in isopropanol and annealing at 140 °C for 25 min in air. One film was retained as-prepared for XPS characterization, and the other was used to fabricate an inverted OPV by adding subsequent layers of P3HT:PCBM ([6,6]-phenyl-C61-butyric acid methyl ester), PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate), and Ag as described elsewhere.[9,13] The inverted OPV exhibited diode-like behaviour under dark and illuminated conditions, as shown in Figure 1. We measured an open circuit voltage (V_{oc}) of 0.591 V, a short-circuit current density (J_{sc}) of 8.54 mA/cm^2, a fill factor of 62%, and a photoconversion efficiency (PCE) of 3.14%. This

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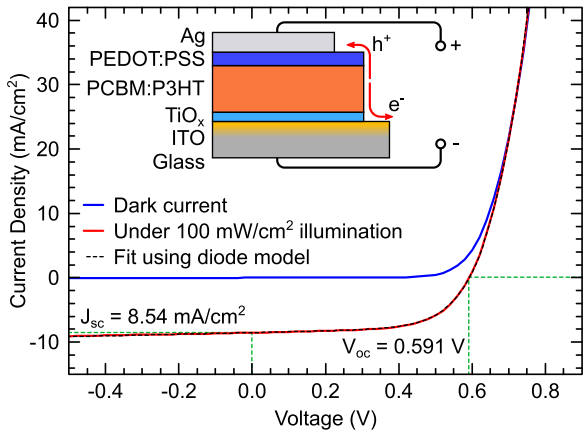

FIG. 1. Illuminated and dark current density–voltage curve for an ITO/TiO_x/P3HT:PCBM/PEDOT:PSS/Ag inverted solar cell. A schematic of the solar cell is also shown.

performance was obtained after "soaking" the OPV under UV-light for 10 min; this step greatly improves the electron carrier selectivity and thus the inverted OPV device performance.[14,15]

The diode-like behaviour of this device is demonstrated by fitting the measured J-V curve to an equivalent circuit model[16] as described by Equation (1)

$$J = J_0\left[\exp\left(\frac{q(V - R_sJ)}{nk_BT}\right) - 1\right] - J_{ph} + \frac{V - R_sJ}{R_{sh}}. \quad (1)$$

In Equation (1), J_{ph} is the photocurrent density, J_0 is the reverse saturation current density, R_s is the series resistance, R_{sh} is the shunt resistance, and n is the ideality factor. The fitted values of $J_{ph} = 8.5\,\text{mA/cm}^2$, $J_0 = 0.98\,\mu\text{A/cm}^2$, $R_s = 0.95\,\Omega\,\text{cm}^2$, $R_{sh} = 790\,\Omega\,\text{cm}^2$, and $n = 2.6$ obtain an excellent match to the measured current density, as shown in Figure 1. Our ideality factor and reverse saturation current density are both larger, and our series resistance is considerably smaller, than those of a conventional P3HT:PCBM OPV.[17] The presence of a TiO_x buffer layer may be responsible for these differences.

To measure the electronic structure of the TiO_x layer in the inverted OPV, we use scotch tape to remove the Ag, PEDOT:PSS, and P3HT:PCBM layers, re-exposing the TiO_x. XPS measurements were made using a PHI 5000 VersaProbe XPS spectrometer (ULVAC Physical Electronics, USA). This apparatus uses Al Kα radiation (1486.6 eV) with a spot size of 100 μm. The chamber pressure during measurements was better than 10^{-7} Pa. Dual channel neutralization was used to compensate for local surface charge generated during the measurement. The XPS spectra are shown in Figure 2(a).

The Ti 2p XPS spectra are shown in Figure 2(b). There is the clear signature of Ti^{3+} visible in the low-energy side of the Ti $2p_{3/2}$ feature in both the as-prepared and extracted TiO_x films. This feature is also present in the low-energy side of the Ti $2p_{1/2}$ feature, although it is harder to see. The energy separation between the Ti^{3+} and Ti^{4+} $2p_{3/2}$ and $2p_{1/2}$ levels are both 5.7 ± 0.1 eV, as previously reported.[1,4,6,9,10] The measured spectra can be accurately reconstructed with using a Shirley background and four fitted Voigt lineshapes corresponding to the $2p_{3/2}$ and $2p_{1/2}$ core levels of Ti^{3+} and Ti^{4+}. These fitted peaks are in excellent agreement with

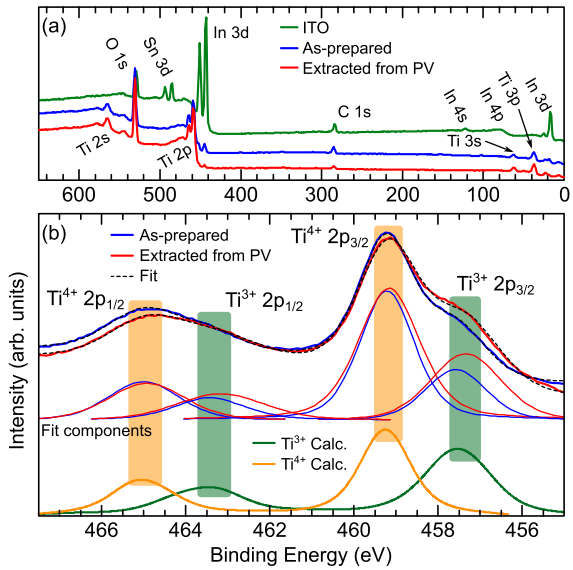

FIG. 2. The (a) survey and (b) Ti 2p XPS spectra TiO_x films. All spectra were calibrated by setting the carbon impurity C 1s core level to 285.0 eV.[18]

simulated XPS spectra from octahedrally coordinated Ti^{3+} and Ti^{4+}, as shown in Figure 2. These simulations were performed using the CTM4XAS program[19] with a 10 Dq value of 2.1 eV and broadened to mimic the experimental resolution. We estimate the Ti^{3+} fraction of the total Ti as 33 ± 1% and 39 ± 1% in the as-prepared and extracted TiO_x films, respectively, using the area of the fitted XPS peaks.

There is negligible difference in the O 1s XPS spectra from both TiO_x films, as shown in Figure 3(a). The O 1s XPS very clearly shows the O^{2-} from TiO_2 at 530.0 eV, and the spectrum has a somewhat extended tail on the high-energy side. A previous report showed clear O 1s XPS features from Ti_2O_3 and OH in a DSSC;[12] we do not observe these here. The high-energy tail in our O 1s XPS is likely due to a mixture of various carbon–oxygen complexes on the surface. This suspicion is verified by examining the C 1s XPS spectra from both TiO_x films, as shown in Figure 3(b). Interestingly, the C 1s XPS of the extracted TiO_x film is essentially identical to that of the as-prepared film, indicating that our scotch tape extraction of the TiO_x film from the OPV removed all of the P3HT:PCBM. Most of the C 1s XPS can be attributed to C-C bonds, although a C-O=C structure and other carbon/oxygen complexes contribute to the high-energy tail of the main C 1s XPS peak.[20]

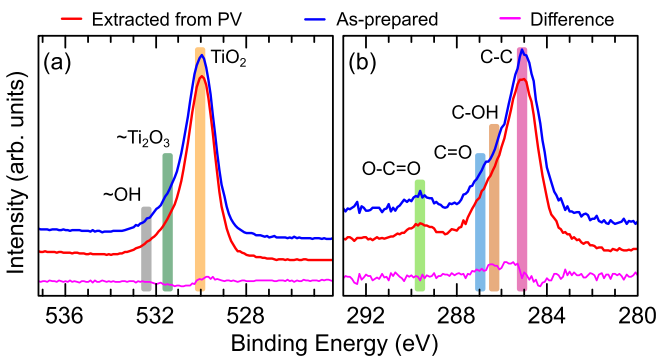

FIG. 3. The normalized (a) O 1s and (b) C 1s XPS spectra from the TiO_x films. The difference between the two spectra is also shown.

The difference in the Ti^{3+} content of the as-prepared and extracted TiO_x films may have three possible origins: (1) it may simply highlight the variability in TiO_x stoichiometry even from films prepared from the same precursors, (2) the interaction between TiO_x and the P3HT:PCBM active layer in the OPV may remove oxygen from the TiO_x layer, (3) the UV soaking step may cause structural changes in the TiO_x leading to more surface Ti^{3+}. We expect that all three of these contribute to the Ti^{3+} content. Residual carbon from the titanium butoxide precursor or from the atmosphere may draw additional oxygen from the TiO_x film,[5] creating many O vacancies. The thermal annealing processing step may result in removing most of these C-O complexes from the surface (as well as surface -OH groups),[6] as the relatively weak C 1s XPS spectra suggest minimal carbon contamination. Adding (and subsequently removing) P3HT:PCBM may create even more O vacancies, while soaking under UV light may cause more interstitial Ti to migrate to the surface.[8] Both of these processes would increase the surface Ti^{3+} fraction, as observed in our XPS measurements of the extracted TiO_x film compared with the as-prepared TiO_x film. We note that the stoichiometries estimated from the XPS measurements are $TiO_{1.8}$ and $TiO_{1.6}$ for the as-prepared and extracted films, respectively (curve-fitting was employed to remove the non-Ti related features in the O 1s XPS, and we used the standard elemental sensitivity factors[18]). On the other hand, our two films exhibit substantial Ti^{3+} content, while other similar inverted OPVs exhibit significantly less Ti^{3+}.[9] It seems that the ambient conditions during device fabrication may have a significant influence on the Ti^{3+} content. Our findings regarding the two films studied herein may suggest, however, that the Ti^{3+} content in an inverted OPV will be slightly increased compared with an as-prepared TiO_x film which has not undergone UV soaking or had an active layer deposited on top but was prepared in the same batch as the OPV. This is an important possibility to consider, as previous XPS studies on OPVs have only examined as-prepared TiO_x films,[1,4,6,9,12,21] and have not extracted the TiO_x from the OPV after operation as we have done here.

Herein we adopt the coherent potential approximation (CPA) to calculate the electronic structure of TiO_x.[22] We start with the local density approximation (LDA) electronic structure of defect-free TiO_2 (using a $2 \times 2 \times 1$ supercell based on the experimental lattice parameters[23]) calculated using the Stuttgart TB-LMTO-ASA code (version 47).[24] The electronic structure of TiO_x is then obtained from the single-site electronic Green's function.

Our calculated valence band electronic density of states (DOS) using CPA is shown in Figure 4 to be in good agreement with our measured XPS spectra, and both reveal defect-related states within the band gap. The mid-gap defect states in our CPA calculation represent 2.1% of the total occupied states in the valence band, while the area under the defect feature is 2.6% and 2.8%, suggesting a stoichiometry of $TiO_{1.85}$ and $TiO_{1.83}$ and a Ti^{3+} fraction of 30% and 34%, in our as-prepared and extracted TiO_x films, respectively. This is in reasonable agreement with our estimates based on the Ti 2p XPS. As mentioned above, comparing the elemental sensitivity-weighted O 1s and Ti 2p XPS intensities gives us $TiO_{1.8}$ and $TiO_{1.6}$ for the as-prepared and extracted TiO_x films, respectively. It therefore seems likely that some of the Ti^{3+} is also due to interstitial Ti.[8] Note that interstitial Ti^{3+} is expected to contribute negligible mid-gap states.[25]

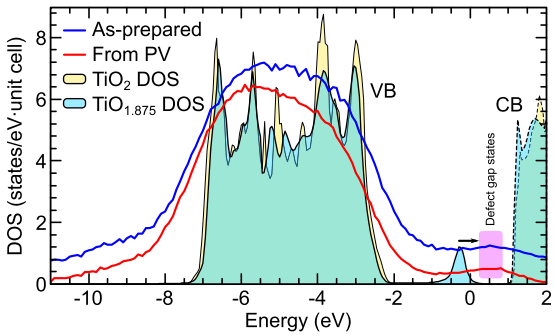

FIG. 4. Valence XPS spectra (Shirley background subtracted) of TiO_x films and calculated electronic DOS. The top of the valence band is set to 0 eV.

We can estimate the number of free electrons at room temperature as $N_d \exp(-\frac{E_c - E_F}{k_B T}) \approx 4 \times 10^{17}\,\mathrm{cm}^{-3}$ in our TiO_x films, where N_d is the number of states in the defect band, $E_c = 1$ eV is the conduction band minimum, and $E_F \approx 0.75$ eV based on the XPS defect gap states shown in Figure 4. This is a fairly substantial level of doping and may greatly enhance the carrier transport in the TiO_x films reported herein compared with stoichiometric TiO_2. This may be the origin of the relatively large reverse saturation current and relatively low series resistance observed in the inverted OPVs under investigation.

To summarize, we have studied the electronic structure of TiO_x in an inverted OPV device using core level and valence XPS and density functional theory (DFT)-CPA calculations. We found that the Ti^{3+} fraction can be obtained from the Ti 2p XPS core level or the total area of the mid-gap states in the valence XPS. The quantity of Ti^{3+} likely depends on the method of synthesis, exposure to oxygen, and UV light-soaking. If these can be carefully controlled, there is the potential for engineering the Ti^{3+}/Ti^{4+} ratio. This is important since the quantity of Ti^{3+} can have a major influence on the availability of free electrons in the TiO_x films.

A final question remains: What is the effect of Ti^{3+} on an OPV device? Compared with TiO_x-based DSSCs or TiO_x + P3HT-based OPVs, J_{sc} and V_{oc} for TiO_x + P3HT:PCBM-based OPVs are quite consistent, as shown in Fig. 5(a). However, this does not mean that Ti^{3+} has no influence on the OPV. For example, we previously reported at TiO_x OPV with a PCE of 3.06% and a Ti^{3+} fraction of roughly 5%.[9]

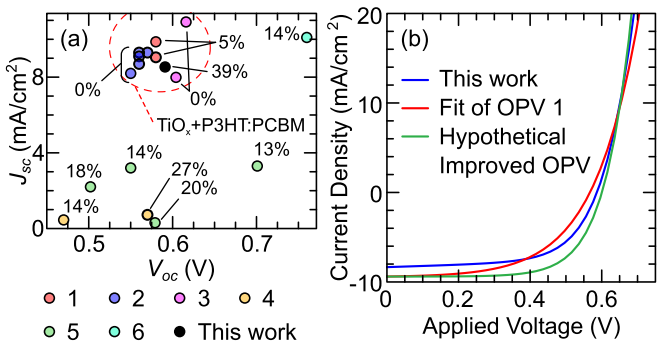

FIG. 5. (a) J_{sc} and V_{oc} for several TiO_x-based OPVs (1,[9] 2,[6] 3,[4] 4[1]) and DSSCs (5,[12] 6[21]). The Ti^{3+} fraction is labelled. (b) The fitted diode-model current density–voltage curves from this work, TiO_x OPV 1,[9] and a hypothetical OPV using the best parameters of the two.

The J-V curve from this OPV can be accurately fit using the diode model (see Fig. 5(b)). Our previous OPV exhibits a better J_{ph} and R_{sh}, while our present OPV exhibits a better J_0 and a better n. Increasing Ti^{3+} content may improve the diode-behaviour of the OPV while simultaneously decreasing the parallel resistance. However if, through carefully engineering the TiO_x layer, one could obtain an OPV with the good diode characteristics of the latter and the good resistance characteristics of the former, this improved OPV would exhibit an increased PCE of 3.9% (see Fig. 5(b)). This is admittedly speculative, but we do expect that increased Ti^{3+} content will have both good and bad effects on the device, and we anticipate that careful engineering of the TiO_x layer may improve device efficiency. There is, therefore, good reason to investigate engineering the Ti^{3+} content in TiO_x electron-selective contacts in OPVs.

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