

Overcoming the Interfacial Photocatalytic Degradation of Nonfullerene Acceptor-Based Organic Photovoltaics by Introducing a UV-A-Insensitive Titanium Suboxide Layer

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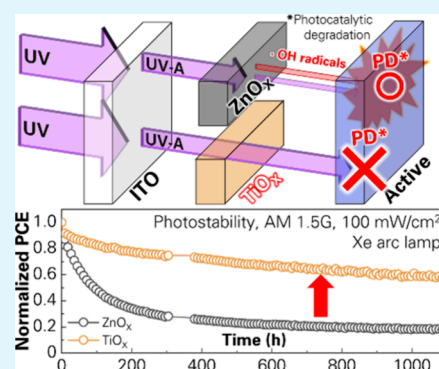
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ABSTRACT: Although recent dramatic advances in power conversion efficiencies (PCEs) have resulted in values over 19%, the poor photostability of organic photovoltaics (OPVs) has been a serious bottleneck to their commercialization. The photocatalytic effect, which is caused by incident ultraviolet-A (UV-A, 320–400 nm) light in the most commonly used zinc oxide (ZnO_x) electron transport layer (ETL), significantly deteriorates the photostability of OPVs. In this work, we develop a new and facile method to enhance the photostability of nonfullerene acceptor-based OPVs by introducing UV-A-insensitive titanium suboxide (TiO_x) ETL. Through an in-depth analysis of mass information at the interface between the ETL and photoactive layer, we confirm that the UV-A-insensitive TiO_x suppresses the photocatalytic effect. The resulting device employing the TiO_x ETL shows excellent photostability, obtaining 80% of the initial PCE for up to 200 h under 1 sun illumination, which is 10 times longer than that of the conventional ZnO_x system (19 h).

KEYWORDS: organic photovoltaics, photostability, photocatalytic effect, metal oxide, titanium suboxide



INTRODUCTION

Despite significant efforts to extend the device lifetime, the photostability of organic photovoltaics (OPVs) remains a challenging barrier to their commercialization. An unwanted decrease in performance occurs during device operation even under inert conditions because OPVs suffer from photo-oxidation of organic materials, morphological reconstruction by heat, interfacial chemical degradation, etc.^{1–5} Among them, the most critical degradation factor is photocatalytic degradation at the interface between the organic photoactive layer and zinc oxide (ZnO_x) electron transport layer (ETL) in inverted OPVs.^{6–9} When light is incident on the device, the portion of ultraviolet light with high energy (UV-B and UV-C, 100–320 nm) is absorbed by and/or reflected from the transparent substrate (indium tin oxide, ITO). Then, the remaining portion of UV (UV-A, 320–400 nm, Figure S1) transmitted through the substrate activates ZnO_x , resulting in the formation of highly reactive species such as hydroxyl radicals ($\cdot\text{OH}$).^{10–13} Consequently, these radicals can decompose the nonfullerene acceptors (NFAs) at the interface, deteriorating the electron-accepting properties of NFAs and gradually decreasing the performance of OPVs.^{12–14}

Several strategies have been introduced to overcome this interfacial photocatalytic degradation in OPVs by using a passivation bilayer, replacing organic ETLs, etc. For example, the passivation bilayer $\text{ZnO}_x/(\text{C}_{60}$ fullerene self-assembled

monolayer) extended the photostability of OPVs by passivating the surface traps at the interface between ZnO_x and the photoactive layer.^{9,15} On the other hand, replacing ZnO_x with NDI-B as an organic ETL in OPVs enhanced the device lifetime by avoiding the photocatalytic process.¹⁶ However, these applications required additional processing steps, including complicated synthetic routes, which caused time consumption and poor reproducibility issues in fabricating OPVs. Therefore, developing an ideal ETL for OPVs that meets the property of facile processability while obtaining high photostability has been a significant challenge for commercializing OPVs.^{17–19}

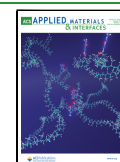
In this work, we successfully enhanced the photostability of NFA-based OPVs by introducing a UV-A-insensitive titanium suboxide (TiO_x) ETL into NFA-based OPVs for the first time. By using Orbitrap/time-of-flight hybrid secondary-ion mass spectrometry (OrbiSIMS), we directly observed that the photocatalytic decomposition started from the interface between the ETL and photoactive layer and that the atomic

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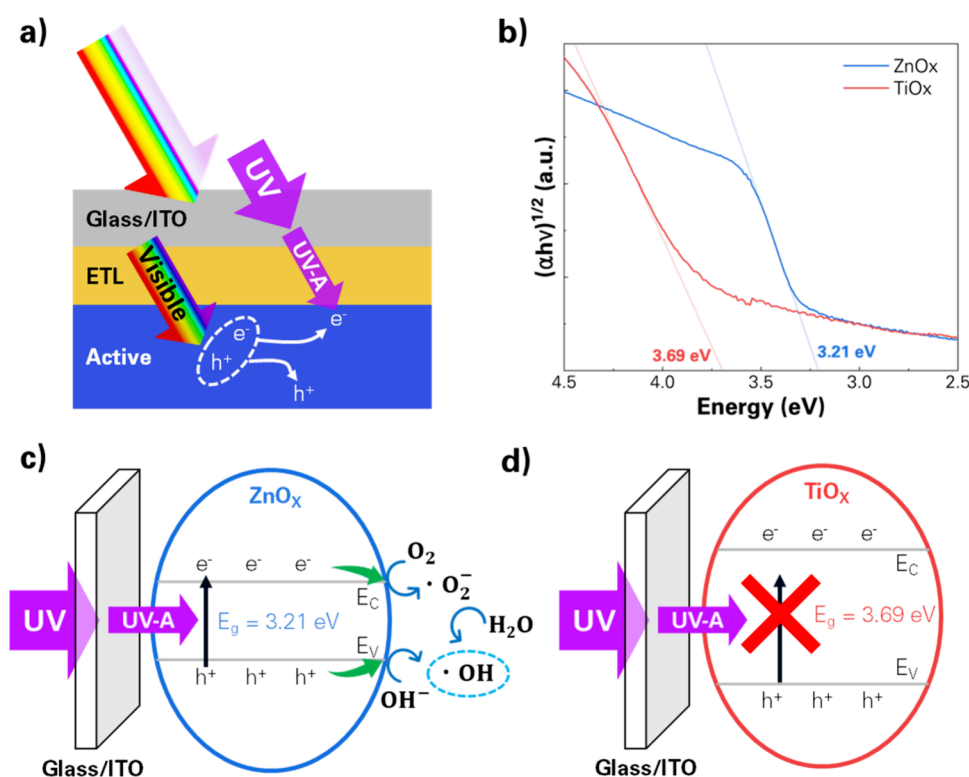


Figure 1. Schematic illustrations of optical interactions in OPVs. (a) Illustration of the incident light path within OPVs. (b) Tauc plots of ZnO_x and TiO_x. Illustration of the photocatalytic process induced by UV-A light incident through the transparent substrate in (c) ZnO_x and (d) TiO_x.

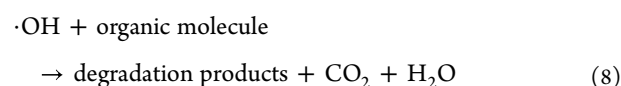
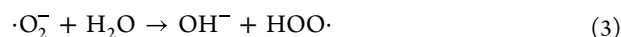
loss of NFAs is much lower in the TiO_x system than in the conventional ZnO_x system. Consequently, we have realized high photostability of OPVs by successfully suppressing the photocatalytic effect in the TiO_x system, obtaining 80% of their initial power conversion efficiency (PCE, T_{80}) for up to 200 h under the measurement conditions of air mass 1.5 global (AM 1.5G) 1 sun irradiation including UV in a nitrogen-filled chamber; the OPV even shows an excellent PCE of 18.07%, which exceeds that of ZnO_x-based OPV (17.79%).

RESULTS AND DISCUSSION

Figure 1 demonstrates a schematic illustration of optical interactions such as light transmission, absorption, and the photocatalytic effect in OPVs, following the optical bandgap of each layer. As shown in Figure 1a, when AM 1.5G simulated light is incident on the glass/indium tin oxide (ITO) substrate, the portion of ultraviolet light with a high energy (>3.67 eV, as shown in Figure S2) is absorbed by and/or reflected from the transparent substrate (indium tin oxide, ITO), and the remaining portion of the UV light (UV-A) is transmitted to the ETL. To estimate a more accurate optical band gap of amorphous metal oxide ETLs, we examine the Tauc plots of ZnO_x and TiO_x as following the eq 1.^{20,21} As demonstrated in Figure 1b, ZnO_x (optical bandgap $E_g \sim 3.21$ eV) is excited by incident UV-A light (<3.67 eV); thus, the electrons from the conduction band (e_{CB}^-) and the holes from the valence band (h_{VB}^+) of ZnO_x should be transported to ITO and the photoactive layer.²² However, intrinsic defects such as oxygen vacancies of the metal oxide become centers that trap the photogenerated electrons, causing the photocatalytic process, as shown in Figure 1c and Figure S3.^{10,23–26} Thus, some photoexcited electrons reduce adsorbed oxygen to produce superoxide ($\cdot O_2^-$), which subsequently produces hydroxyl

radicals (eqs 1–4).²⁷ On the other hand, holes from the valence band oxidize nearby water and hydroxyl anions to produce hydroxyl radicals (eqs 5 and 6).²⁸ These highly reactive hydroxyl radicals attack the NFA at the interface between the bulk-heterojunction photoactive layer and metal oxide ETL (eq 7).^{10–12} Consequently, the electron acceptors gradually lose their electron-accepting property, which results in a slightly decreased photostability of OPVs in terms of the PCE.^{12–14}

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (1)$$



To suppress this photodecomposition, we developed a UV-A-insensitive TiO_x ETL for NFA-based OPVs by a novel blending method. Although the wide bandgap TiO_x ETL was already reported for OPVs in previous works, the synthetic route for its precursor solution, which followed the conventional synthetic process that uses a three-necked flask for reflux

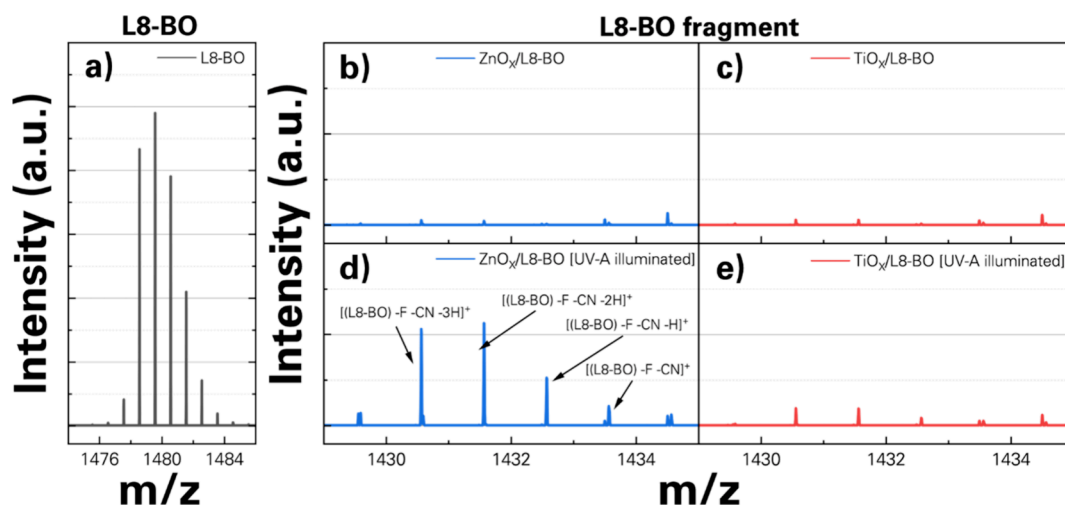


Figure 2. MS of L8-BO ions and fragment ions. (a) L8-BO ions and (b–e) L8-BO fragment ions. L8-BO fragment ions of (b, c) as-cast metal oxide/L8-BO samples and (d, e) metal oxide/L8-BO samples illuminated by 365 nm UV-A light for 60 h. [The scales of the Y-axes in panels b–e are equivalent].

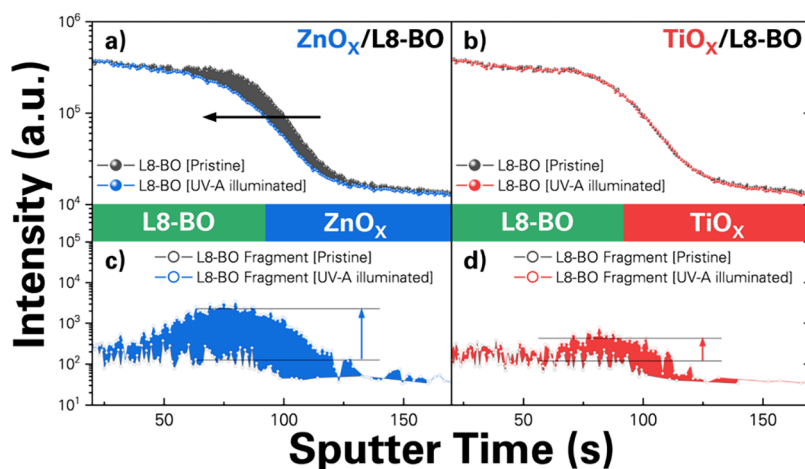


Figure 3. Depth profile spectra before and after 365 nm UV-A light illumination for 60 h. (a, b) Intensity for L8-BO ions in metal oxide/L8-BO. (c, d) Intensity for L8-BO fragment ions in metal oxide/L8-BO samples. [The scales of the Y-axes in panels a,b and c,d are equivalent].

in Ar-filled conditions, has problems such as being time-consuming and having poor reproducibility.^{24,25,29} Moreover, the fabricated TiO_x ETL showed a notorious light-soaking problem that resulted in a decreased PCE of OPVs, thereby limiting its usage to only fullerene-based OPVs.^{30–34} Herein, by adding a small amount of water during the blending process for preparing the TiO_x precursor solution, we induced a prehydrolysis step to increase the Ti–O–Ti connectivity, which led to a dense gel network in a film form.^{35–38} As shown in Figure S4, X-ray photoelectron spectroscopy (XPS) spectra show that the intensity of Ti^{3+} ions, which is correlated to the defect in the TiO_x film, decreased with the addition of water in Ti 2p spectra.^{39–41} Accordingly, the intensity of lattice oxygen (O_L) increases and the intensity of –OH bond and oxygen vacancy (O_V) decreases with the addition of water in O 1s spectra.^{39,40,42} By using TiO_x as the ETL, we obtained high-performance NFA-based OPVs, even showing no light-soaking problem (see the detailed information in the device performance part in the experimental section and in the Supporting Information). As shown in Figure 1b, we confirmed that the newly fabricated TiO_x film ($E_g \sim 3.68$ eV) has a higher optical bandgap than that of the glass/ITO substrate (3.67 eV).

Therefore, we expected that TiO_x could be insensitive to UV-A light (<3.67 eV) incident through the transparent substrate by suppressing the photocatalytic effect (Figure 1d).

To directly confirm the photocatalytic decomposition of the electron acceptor, mass spectra (MS) of the photodegraded samples were obtained by OrbiSIMS, as shown in Figure 2. The MS obtained by the integration of depth profile information from the photoactive layer to the ZnO_x at a full range is demonstrated in Figure S5. The high-efficiency organic electron acceptor L8-BO was chosen for the samples, and then the metal oxide/L8-BO samples were illuminated by 365 nm UV-A light for 60 h. As shown in Figure 2a, the OrbiSIMS analysis confirmed that the peak at an m/z ratio of 1479.58 indeed corresponded to an ion produced from L8-BO.⁴³ Remarkably, we found that fragments appeared in the $\text{ZnO}_x/\text{L8-BO}$ sample after photodegradation, with peaks at m/z ratios ranging from 1429 to 1435 (Figure S5). These results are demonstrated in Figure 2b–e, illustrated as blue lines for $\text{ZnO}_x/\text{L8-BO}$ and red lines for $\text{TiO}_x/\text{L8-BO}$. Before photodegradation, fragments of L8-BO on metal oxides were barely detected (Figure 2b,c). However, L8-BO fragments were abundantly produced after UV-A illumination, especially in the

Table 1. Summary of the Device Parameters of OPVs with Different Metal Oxide ETLs

ETL	V_{oc}^a (V)	J_{sc}^a (mA/cm ²)	integrated J_{sc}^a (mA/cm ²)	FF ^a (%)	PCE ^a (%)
ZnO _x (control)	0.889 (0.888 ± 0.003)	26.45 (26.07 ± 0.25)	24.61	75.74 (76.06 ± 0.18)	17.79 (17.62 ± 0.12)
TiO _x	0.888 (0.882 ± 0.004)	26.89 (26.99 ± 0.13)	25.36	75.69 (75.22 ± 0.46)	18.07 (17.90 ± 0.16)

^aAverage parameters in parentheses are obtained from at least 10 devices.

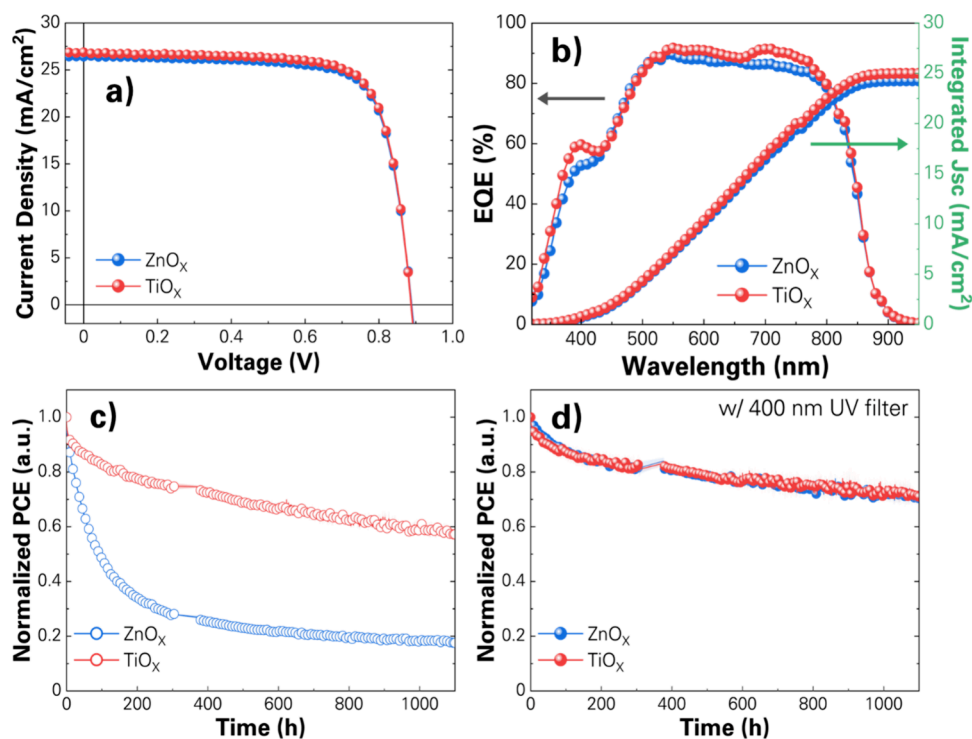


Figure 4. Characteristics of OPVs with the ZnO_x ETL (blue) and TiO_x ETL (red): (a) current density–voltage (J – V) curves of the OPVs and (b) EQE and integrated J_{sc} of the OPVs. Photostabilities of OPVs under AM 1.5G 100 mW/cm² light illumination by a xenon arc lamp (c) without a UV cutoff filter and (d) with a 400 nm UV cutoff filter.

ZnO_x/L8-BO sample, as shown in Figure 2d. In contrast, in the case of the TiO_x/L8-BO sample, there was no significant amount of fragments produced with peaks in the same range of m/z ratios. The observed slight increase in fragment intensity on TiO_x/L8-BO samples, as illustrated in Figure 2e, is attributed to photocatalytic degradation originating from a small portion of high-energy radiation reaching the TiO_x (>320 nm, as shown in Figure S1). Therefore, these MS data are direct evidence that the photocatalytic effect was suppressed by TiO_x under incident UV-A light, which is consistent with the absorption spectra (Figure S6). Moreover, we conclude that L8-BO is decomposed by the photocatalytic effect with the loss of some atoms (H, F, CN) while maintaining the backbone of the molecule.

To gain more detailed information on photodegradation in the devices, we performed depth profiling on the ZnO_x/L8-BO and TiO_x/L8-BO films. Figure 3 shows depth profile overlays of pristine L8-BO (black line), 365 nm UV-A-illuminated ZnO_x/L8-BO (blue line), and TiO_x/L8-BO (red line) according to the L8-BO ions (filled circles) and fragment ions (empty circles) collected by OrbiSIMS. To compare the photocatalytic effect, the intensities for the L8-BO ions (Figure 3a,b) and fragment ions (Figure 3c,d) were fixed at the same scale for the Y-axis. As shown in the depth profiles, the tendencies of photocatalytic decomposition differed between the metal oxides. The intensity for L8-BO on the ZnO_x films significantly decreased after UV-A irradiation (Figure 3a).

Remarkably, even the intensity for L8-BO near the interface between the metal oxide and electron acceptor decreased (Figure S7). Furthermore, the detected L8-BO fragments increased after UV-A illumination at the interface rather than in the bulk (blue arrow in Figure 3c and Figure S8). In contrast, the intensity for L8-BO on the TiO_x films remained similar, and the fragments did not substantially increase after UV-A irradiation, as shown in Figure 3b,d. Based on these results, we clearly infer that photocatalytic decomposition starts at the interface and UV-A-insensitive TiO_x enhances the photostability by suppressing interfacial photochemical degradation.

To explore the impact of TiO_x on photostability, OPVs with an inverted structure consisting of glass/ITO/metal oxide (TiO_x or ZnO_x)/photoactive layer (PM6:L8-BO)/molybdenum suboxide (MoO_x)/Ag were fabricated (see the detailed fabrication method in the experimental section and in the Supporting Information). The current density–voltage (J – V) characteristics of the OPVs were measured under AM 1.5G 1 sun illumination (100 mW/cm²). The statistical photovoltaic parameters are summarized in Table 1, which were calculated from at least 10 devices (the information about the other photoactive layers, PM6:Y6 and PTB7-th:IEICO-4F, is demonstrated in the Supporting Information, Figure S9 and Table S1). As demonstrated in Figure 4a, wide-band gap TiO_x (red line with circles) yielded the best PCE of 18.07% with an open-circuit voltage (V_{oc}) of 0.888 V, a current density (J_{sc}) of

26.89 mA/cm², and a fill factor (FF) of 75.69%. Surprisingly, the performance of the TiO_x-based OPV was even higher than that of the ZnO_x-based OPV (control; black line with circles), for which the PCE was 17.79% (V_{oc} of 0.889 V, J_{sc} of 26.45 mA/cm², and FF of 75.74%). Moreover, note that our optimized TiO_x blending system successfully eliminates the light-soaking feature, which is one of the biggest issues causing this material to not be commonly used for NFA-OPVs (the J - V curve of the light-soaked device is demonstrated in the Supporting Information, Figure S10 and Table S2). We believe that the light-soaking effect was suppressed because of the low defect density and reduced work function of our optimized TiO_x, as shown in Figures S4 and S11 and Table S3. Besides, we attribute that the slightly decreased V_{oc} is derived from the higher work function of TiO_x. As shown in Figure S12, ZnO_x has more ohmic contact with the L8-BO than TiO_x, which results in a slightly high V_{oc} .⁴⁴ Meanwhile, We believe that the increased J_{sc} in TiO_x-OPV is derived from the higher refractive index of TiO_x.^{45,46} The higher refractive index of TiO_x induced high transmittance in the ETL, resulting in more light absorption from the photoactive layer. Moreover, as shown in Table S4, the optimized TiO_x film exhibits the highest mobility with a thickness of 10 nm (Figure S13). Thereby, J_{sc} is slightly increased in TiO_x-OPV, which is consistent with the integrated current density based on the external quantum efficiency (EQE) shown in Figure 4b (25.36 mA/cm² for the TiO_x-based OPV and 24.61 mA/cm² for the control device).⁴⁷ Furthermore, we attribute that the enhancement in photocurrent around 400 nm in EQE of TiO_x-OPV is derived from the less absorption of TiO_x, as shown in Figure S14.

To evaluate the photostability of each metal oxide ETL system, fabricated OPVs were placed in an environment-controlled chamber after checking the PV performance. The photostability of the devices was measured using the laboratory simulation protocols of the International Summit on Organic Photovoltaic-Light-Soaking Tests (ISOS-L1) under AM 1.5G 1 sun illumination (100 mW/cm²) by a xenon arc lamp, and the source was calibrated by a calibrated silicon solar cell from Newport.^{48,49} As demonstrated in Figure 4c, the control device (blue line with hollow circles) rapidly deteriorated, showing a T_{80} of 19 h. In contrast, the TiO_x-based OPV (red line with hollow circles) retained the initial performance for more than 10 times longer than the control device (T_{80, TiO_x} : 200 h) and maintained a photostability of 60% of the initial PCE after 1000 h (see the detailed photostability of each parameter in the Supporting Information, Figures S15 and S16). The sudden drop in PCE in the beginning seems to be the UV-induced photocatalytic burn-in, which derived from the reduction in charge extraction efficiency of the devices with exhibited decreased V_{oc} , J_{sc} , and FF, as shown in Figure S15.^{50,51} Furthermore, we adopted a 400 nm UV cutoff filter (Figure S17) in the middle of the light irradiation spectrum within the devices to check the influence of the photocatalytic effect. When the filter was used, OPVs with each metal oxide ETL showed similar photodegradation tendencies during 1000 h under AM 1.5G 1 sun illumination (Figure 4d). Consequently, we can state that the photodecomposition induced by the photocatalytic effect was obviously suppressed by the UV-A-insensitive TiO_x while showing a high PCE of the OPV. Based on our results, we believe that, in addition to our photostable interfacial engineering technique, the development of additional stability research on morphology reconstruction

by heat and encapsulation could synergistically lead to further improvements in the commercialization of OPVs.

CONCLUSIONS

In conclusion, we successfully suppressed the photocatalytic degradation of the electron acceptor L8-BO by introducing a UV-A-insensitive TiO_x ETL into an NFA-based OPV, which is fabricated by a novel and facile blending method. The MS of the metal oxide/L8-BO samples indicated that the photodegradation of OPVs was significantly influenced by the photocatalytic effect of ZnO_x induced by the incident UV-A light in real operation, while not much degradation occurred in the TiO_x system. Moreover, the depth profile of metal oxide/L8-BO films indicated that the photocatalytic effect started from the interface between the ETL and photoactive layer, with a small amount of loss of atoms in the end group moiety of the photodegraded L8-BO. The resulting photostability of the TiO_x-based OPV is extended to 10 times longer (T_{80, TiO_x} : 200 h) than that of the conventional ZnO_x ETL (T_{80, ZnO_x} : 19 h) by avoiding photocatalytic degradation, and the OPV even shows a slightly higher PCE of 18.07% (control device, 17.79%) with no light-soaking problem. Our results are expected to help solve the stability issues for commercializing OPVs and provide insight into related research fields.

EXPERIMENTAL SECTION

Materials. Titanium(IV) isopropoxide (Ti[OCH(CH₃)₂]₄, 99.999% trace metal basis), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, puriss. p.a., ACS reagent, ≥99.0%), diethanolamine (HN-(CH₂CH₂OH)₂, 98.0%), ethanolamine (NH₂CH₂CH₂OH, ACS reagent, ≥99.0%), and isopropyl alcohol ((CH₃)₂CHOH, anhydrous, 99.5%) were purchased from Sigma-Aldrich to prepare electron transport layer (ETL) precursor solutions. Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene)-alt-(5,5'-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PM6), 2,2'-(2,2',2'')-(12,13-bis(2-ethylhexyl)-3,9-(2-butyloctyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-*e*]-thieno[2',3':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]-thieno[3,2-*b*]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (L8-BO), and 2,2'-(2,2',2'')-(12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2',3':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (Y6) were purchased from Solarmer. Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]-dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]-thiophene)-2-carboxylate-2,6-diyl)] (PTB7-th) and 2,2'-(2,2',2'')-(4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (IEICO-4F) were purchased from 1-Material. 1-Chloronaphthalene (C₁₀H₇Cl, technical grade) and diiodomethane (CH₂I₂, 99%) were purchased from Sigma-Aldrich to prepare the bulk-heterojunction (BHJ) solution for the photoactive layer in organic photovoltaics (OPVs). A zinc oxide (ZnO) solution was blended with zinc acetate dihydrate:ethanolamine:isopropyl alcohol at a molar ratio of 1:1.8:116. A titanium suboxide (TiO_x) solution was blended with titanium(IV) isopropoxide:diethanolamine:isopropyl alcohol:water at a molar ratio of 1:2:20:0.5, stirred for 1 h, and then diluted with anhydrous isopropyl alcohol at a volume ratio of 1:200.

Device Fabrication. Metal oxide/electron acceptor films were prepared on quartz glass substrates for UV irradiation photostability tests and on glass/ITO substrates for mass spectrometry and depth profiling. The inverted structure OPVs were fabricated with the architecture ITO/metal oxide (TiO_x or ZnO_x)/photoactive layer/

MoO_x/Ag. The metal oxide ETL was deposited on UV-ozone-treated ITO substrates by spin-coating at 5000 rpm for 20 s, with thermal annealing at 200 °C for ZnO_x and 120 °C for TiO_x for 10 min. Then, the substrates were transferred into a nitrogen-filled glovebox. The PM6:L8-BO photoactive layer was fabricated by spin-casting the BHJ solution (dissolved in chloroform, D:A ratio of 1:1.2, concentration of 17.6 mg/mL, 0.25 vol % diiodomethane added) at 3000 rpm for 25 s. The PM6:Y6 photoactive layer was fabricated by spin-casting the BHJ solution (dissolved in chloroform, D:A ratio of 1:1.2, concentration of 17.6 mg/mL, 0.5 vol % 1-chloronaphthalene added) at 3000 rpm for 25 s. The PTB7-th:IEICO-4F photoactive layer was fabricated by spin-casting the BHJ solution (dissolved in chlorobenzene, D:A ratio of 1:1.5, concentration of 25 mg/mL, 4 vol % 1-chloronaphthalene added) at 3500 rpm for 30 s, and then the fabricated films were thermally annealed at 100 °C for 10 min. Afterward, for the deposition of the hole transport layer and top electrode, the fabricated samples were transported to the thermal evaporator. Finally, 5 nm of MoO_x and 100 nm of Ag were sequentially deposited under high-vacuum conditions ($\times 10^{-6}$ Torr).

Characterization. Ultraviolet (UV) illumination was performed by using a 365 nm UV lamp (VL-6LC, Vilber Lourmat) with an intensity of 610 μ W/cm². The absorption spectra were obtained using a UV–vis–NIR spectrophotometer (Cary 5000 UV–vis–NIR, Agilent Technologies, Inc.). The X-ray photoelectron spectrometry (XPS) spectra and ultraviolet photoelectron spectrometry (UPS) spectra were obtained by using a Nexsa G2 Surface Analysis System (Nexsa, Thermo Fisher Scientific Inc.). The current density–voltage (*J*–*V*) curves of the PV devices were measured by a Keithley 2420 source/meter unit, with a solar simulator (Sol 3A, xenon arc lamp, class AAA, Newport Corp.) providing air mass 1.5 global (AM 1.5G) irradiation with an intensity of 100 mW/cm². The solar simulator was calibrated by using a certified reference standard Si photodiode (Newport Corp.). External quantum efficiency (EQE) measurements were conducted by using a quantum efficiency (QE) measurement system (Quant X-300, Newport Corp.), with cross-checking of the photocurrent and a chopping frequency of 100 Hz. The QE was calibrated by using a 603621 calibrated reference detector (Newport Corp.). Mobility was calculated by using a hall-effect measurement system (HL5500PC, Accent Optical Technologies). Thickness values of metal oxide films were measured by atomic force microscopy (XE-100, Park Systems). Work functions of the metal oxide films were carried out with a Kelvin probe measurement system (KP6500, McAllister Technical Services). The photostability of the OPVs was measured simultaneously under a large solar simulator (WXS-450S-65, xenon arc lamp, class AAA, AM 1.5G, WACOM Electric Co., Ltd.) within the environment-controlled customized chamber to control the measurement conditions and maintain approximately 25 °C in an inert atmosphere (through nitrogen purging and water cooling). The mass spectra and depth profile were obtained by using Orbitrap/time-of-flight hybrid secondary-ion mass spectrometry (OrbiSIMS) with an M6 hybrid system (ION-TOF GmbH, Münster, Germany) at the Korea Basic Science Institute Busan Center using a pulsed 20 keV Ar₂₀₄₃ primary beam with a current of 115 pA. The secondary-ion mass spectrum was obtained in positive mode for an area of 300 μ m $\times$ 300 μ m, and the sputtered area was 420 μ m $\times$ 420 μ m for each sample. The photodegraded samples for MS and depth profile were prepared following the structure of ITO/ZnO_x or TiO_x/L8-BO under a 365 nm UV lamp in an N₂-filled glovebox.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.3c15801>.

Experimental section (materials, detailed information on device fabrication and characterizations), additional schemes, tables, and figures (UV–vis spectra, mass spectra, *J*–*V* curves, and photostability plots) (PDF)

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Notes

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