Supporting Information

High-Efficiency Inverted Organic Solar Cells with Polyethylene oxide-Modified Zn-doped TiO₂ as Interfacial Electron Transport Layer

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Experimental section

Synthesis of Polyethylene oxide (PEO)-modified Zn-doped TiO$_2$ nanocrystalline thin films: In the present study, PEO-modified Zn-doped TiO$_2$ nanocrystalline thin films have been prepared using sol-gel spin coating method. Titanium (IV) butoxide (Ti(OCH$_2$CH$_2$CH$_2$CH$_3$)$_4$) (0.45M) and zinc acetate dihydrate (Zn(CH$_3$COO).2H$_2$O) (0.01M) were dissolved in a mixture of 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH) and acetylacetone (CH$_3$COCH$_2$COCH$_3$) (0.45M) at room temperature. The resultant solution was stirred for 1h to yield a homogeneous, clear and transparent (light yellowish color) solution using magnetic stirrer. Polyethylene oxide (PEO) (0.01 wt.%, 0.05 wt.%, 0.1 wt.% and 0.3 wt.%) was dissolved in chlorobenzene. The PEO solution was slowly added to Zn-doped TiO$_2$ sol and was stirred for 2h to obtain the final sol ready for deposition of thin films. The spin coating method was used to prepare thin films of PEO-modified Zn-doped TiO$_2$ onto ITO substrates using the prepared sol. PEO-modified Zn-doped TiO$_2$ thin films of thickness 30 nm was formed after post annealing at 500 °C for 1h and these films form the PEO-modified Zn-doped TiO$_2$ nanocrystalline thin films.

Device fabrication and characterization: Inverted organic solar cells (IOSCs) were constructed with a device structure of ITO/PEO:Zn-doped TiO$_2$ (ZTO)/active layer/MoO$_3$/Al. Patterned ITO-coated glass substrates were cleaned by a sequence of sonication in acetone, isopropyl alcohol and deionized water respectively for 15 minutes and UV-ozone cleaning for 10 minutes. A thin layer of PEO-modified ZTO (30 nm) was spin coated onto the ITO substrates and annealed at 500 ºC for 2 hours in air. The PEO-modified ZTO substrates were transferred into a glove box. The PTB7:PC$_{71}$BM blend solution was prepared with a weight ratio of 1:1.5 in a mixed solvent of chlorobenzene/1,8-diiodooctane (97:3 vol.%). The active layer (PTB7:PC$_{71}$BM) was then spin-coated on the PEO-modified ZTO layer and the thickness was about 80 nm. After that the organic layer was slowly dried in vacuum, a layer of MoO$_3$ (10 nm)/Al (100 nm) as electrode was thermally evaporated on top of the
active layer through a shadow mask under a pressure of \(\sim 10^{-6}\) Torr. The effective area of the device was measured to be 0.0196 cm\(^2\).

Ultraviolet photoelectron spectroscopy (UPS) measurement was performed using AXIS Ultra DLD (KRATOS Inc.) with He I (21.2 eV) as monochromatic light source. X-ray photoelectron spectroscopy (XPS, AXIS-HSi) spectra was used to identify the surface elements and their chemical state. Photoluminescence (PL) spectra of the samples were measured using a Monochromator (SP2150i) and an excitation wavelength 375 nm. Surface topography was studied using atomic force microscopy (Park systems, XE-100). The optical properties were studied using the absorbance spectra recorded using Beckman DU-70 spectrophotometer. The thickness of the films were measured using a 10 DektakXT surface profiler. The electrical resistivity was measured by a four-point probe method. The mobility was measured by bottom-gate top-contact thin film transistor (TFT) method with semiconductor parameter analyzer (Agilent 4155C). Current density – voltage (J-V) characteristics of the devices were recorded using a Keithley 237 source measurement unit using a 100 mW/cm\(^2\) AM 1.5G solar simulator (Newport, 91160A). Light intensity was calibrated using a standard silicon solar cell as a reference. The incident photon to charge carrier efficiency (IPCE) spectra of the devices were recorded using a lock-in amplifier (Model 7265, Signal Recovery) and a monochromatic light from a xenon lamp through the monochromator (SpectroPro-150, Acton Research Corporation).
Figure S1. UPS spectra of (a) TiO$_2$, 0.05wt.% PEO:TiO$_2$ and (b) ZTO, 0.05wt.% PEO:ZTO films.
Figure S2. Absorption spectra of (a) TiO$_2$, 0.05wt.% PEO:TiO$_2$ and (b) ZTO, 0.05wt.% PEO:ZTO films.
Table S1: Valance band, conduction band and band gap of TiO₂, 0.05wt.% PEO:TiO₂, ZTO and 0.05wt.% PEO:ZTO films.

<table>
<thead>
<tr>
<th>ETLs</th>
<th>Valence band maximum (VBM) [eV]</th>
<th>Conduction band minimum (VBM) [eV]</th>
<th>Band gap (Eg) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>-7.66</td>
<td>-4.46</td>
<td>3.20</td>
</tr>
<tr>
<td>0.05 wt.% PEO: TiO₂</td>
<td>-7.61</td>
<td>-4.41</td>
<td>3.20</td>
</tr>
<tr>
<td>ZTO</td>
<td>-7.90</td>
<td>-4.60</td>
<td>3.30</td>
</tr>
<tr>
<td>0.05 wt.% PEO: ZTO</td>
<td>-7.92</td>
<td>-4.62</td>
<td>3.30</td>
</tr>
</tbody>
</table>
Figure S3. XPS spectra of TiO$_2$ and ZTO films (a) Ti2p, (b) O1s and (c) Zn2p
Figure S4: Absorption spectra of TiO$_2$ and ZTO films
The mobility has been measured by bottom-gate top-contact thin film transistor (TFT) method. The TFT device structure is shown in figure S5; SiO$_2$ was used as the gate dielectric layer, and Al was used as the source/drain electrode. Transfer characteristics of the TiO$_2$ and ZTO thin film transistors (TFTs) are shown in figure S5. The mobility TiO$_2$ and ZTO thin films are $3.15 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $25.320 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. 

Figure S5. TFT device structure and transfer characteristics of TiO$_2$ and ZTO TFTs
Figure S6. (a) Illuminated J-V, (b) dark J-V characteristics and (c) IPCE spectra of PTB7:PC$_{71}$BM based IOSCs with ETLs of TiO$_2$ and PEO:TiO$_2$. 
Figure S7. (a) Illuminated J-V, (b) dark J-V characteristics and (c) IPCE spectra of PTB7:PC$_{71}$BM 25 based IOCs with ETLs of ZTO and PEO:ZTO.
Figure S8. The stability of the PTB7:PC$_{71}$BM based inverted device fabricated using TiO$_2$, 0.05 wt.% PEO:TiO$_2$, ZTO and 0.05 wt.% PEO:ZTO as an electron transport layer

The use of metal oxides on both sides of the PTB7:PC$_{71}$BM layer prevents the diffusion of moisture into the active layer. The stability of the inverted PTB7:PC$_{71}$BM solar cells (with MoO$_3$ as the hole transport layer and TiO$_2$, 0.05 wt.% PEO:TiO$_2$, ZTO or 0.05 wt.% PEO:ZTO as the electron transport layer) is shown in Figure S8. The solar cells were exposed continuously to air at room temperature (without any encapsulation barrier). We observed that TiO$_2$, 0.05 wt.% PEO:TiO$_2$ based devices almost retain its original efficiency even after 30 days under ambient conditions with reduction of power conversion efficiency (PCE) from 6.98 to 6.72 % and 7.51 to 7.30 %, while for the device fabricated using ZTO and 0.05 wt.% PEO:ZTO ETL the PCE decreased 7.67 to 7.32 % and 8.10 to 7.82 % under the same conditions. This clearly shows that TiO$_2$, PEO:TiO$_2$, ZTO and PEO:ZTO based devices exhibit good stability.
Figure S9: PL spectra of TiO₂ and PEO:TiO₂ films
**Figure S10:** PL spectra of ZTO and PEO:ZTO films
20 Figure S11: AFM images of (a) TiO$_2$ and PEO:TiO$_2$ films (b) 0.01 wt.% PEO, (c) 0.05 wt.% PEO, (d) 0.1 wt.% PEO, (e) 0.3 wt.% PEO
Figure S12: AFM images of (a) ZTO and PEO:ZTO films (b) 0.01 wt.% PEO, (c) 0.05 wt.% PEO, (d) 0.1 wt.% PEO, (e) 0.3 wt.% PEO