SUMMARY

Organic photovoltaics (OPVs) have attracted considerable attention in recent years. Most reported strategies are from the perspective of the active layers to control the morphology of the donor/acceptor blend, with few methods focusing on modifying the transporting layers. Here, we develop a facile method to enhance both the thermal stability and efficiency of OPVs simultaneously from the perspective of the electron-transporting layer (ETL). Compared with traditional planar ETLs used in OPVs, our mesoporous ETL is designed to serve as a rigid scaffold to inhibit polymer diffusion upon heating. Furthermore, this structure creates more surface-area contact between the active layer and the ETL, potentially enhancing charge-extraction efficiency. As a result, the power-conversion efficiency (PCE) with this structure was enhanced by 11% relative to the planar structure. After being subjected to thermal stability test, the PCE of the mesoporous structure retained 69% of its original value.

INTRODUCTION

The 21st century has seen a shift in energy consumption patterns toward the development of clean, renewable energy, motivated by the scarcity and depletion of finite fossil energy sources. In particular, solution-processed organic photovoltaics (OPVs) have attracted considerable attention due to their unique combination of advantages, such as their light weight, high mechanical flexibility, semi-transparency, and compatibility with roll-to-roll processing as compared with other thin-film technologies.\(^{1-10}\) Tremendous progress has been made in the last 5 years, with record power-conversion efficiencies (PCEs) exceeding 13% reported by multiple groups.\(^{11-13}\)

To date, a host of methods have been demonstrated to enhance the PCEs of OPVs,\(^ {14,15}\) including designing and synthesizing new n-type or p-type organic semiconductor materials with broad photon absorption spectra and outstanding electric properties,\(^ {13,16-22}\) introducing additives to control the morphology,\(^ {23-25}\) utilizing solvent or postannealing treatments,\(^ {26,27}\) implementing rational buffer layers between the electrodes and active layers,\(^ {28,29}\) incorporating a third component as part of a ternary system as the active layer,\(^ {30,31}\) and using different device architectures, such as the inverted structure.\(^ {32-34}\)

In parallel with boosting the PCE, achieving high device stability is the other important consideration for OPVs.\(^ {35}\) Recently, a variety of strategies to improve device stability have been proposed and examined, such as designing rational donor and acceptor molecular structures,\(^ {33,34}\) using a third component to enhance stability,\(^ {35}\)
and using non-fullerene materials to suppress the aggregation of fullerene acceptors such as [6,6]-phenyl-C61-butyric-acid methyl-ester (PCBM) under light, heat, and other conditions.\(^3\) The main goal underlying most of these developments is to improve the thermal stability of OPVs, arguably the most important consideration to enable the commercialization of OPVs, since solar cells operate at elevated temperatures. Due to the metastable nature of the donor/acceptor blend, the polymers diffuse more readily, and there is increased aggregation of the fullerene at higher temperatures.\(^3\) One of the most tried and tested methods in a bid to limit this diffusion and aggregation, and hence improve thermal stability, consists of morphological control of the active layer. As such, most reported strategies are from the perspective of the active layers, with few methods focusing on modifying the transporting layers.

Herein, we develop a facile method to enhance both the thermal stability and efficiency of OPVs simultaneously from the perspective of the electron-transporting layer (ETL). Compared with traditional planar and compact ETLs used in OPVs (Figure 1A), our mesoporous ETL is designed to serve as a rigid scaffold to inhibit polymer diffusion and the aggregation of the fullerene acceptors upon heating, owing to its high-temperature sintering process (Figure 1B). Furthermore, the rigid scaffold structure creates more surface-area contact between the active layer and the ETL, potentially enhancing charge-extraction efficiency.

**RESULT AND DISCUSSION**

The chemical structures of the materials used as the active layer in this work are shown in Figure 1C. Medium-bandgap polymer PffBT4T-C\(_9\)C\(_{13}\)\(^3\) is used as the
donor and PC71BM is used as the acceptor. To investigate the effects of this rigid scaffold structure, OPVs with solution-processed mesoporous titanium dioxide (mp-TiO2), compact titanium dioxide (c-TiO2), and zinc oxide (ZnO) were systematically studied. The surface morphology of the three different ETLs was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). As shown in Figures 2A, 2B, 2D, and 2E, the surfaces of ZnO and c-TiO2 are uniform and smooth. The root-mean-square (RMS) roughness values of ZnO and c-TiO2 are 1.35 and 1.55 nm, respectively. For the mp-TiO2, the mesoporous surface consisting of small particles is shown in Figures 2C and 2F, with a RMS roughness value of 27.2 nm. Such a morphological feature creates more interface surface area between the ETL and the active layer.

Figure 3 shows the current density-voltage (J-V) curves and the external quantum efficiency (EQE) spectra of devices based on ZnO, c-TiO2, or mp-TiO2 under the illumination of an AM 1.5G solar simulator. The thermal stability tests were carried out at 120 °C in a nitrogen atmosphere for 60 min. The results are displayed as graphs of average PCE as a function of annealing time, as shown in Figure 3C, while Table 1 summarizes the average and maximum device performance values achieved for PFBT4T-C4C13:PC71BM with ZnO, c-TiO2, or mp-TiO2 and the average and the best device characteristics of PFBT4T-C4C13:PC71BM with ZnO, c-TiO2, or mp-TiO2 as ETLs before and after a thermal stability test. The averages were calculated from ten individual devices. The thickness of the active layer is around 250–350 nm, so that the mp-TiO2 layer can be fully covered by the active layer, which ensures the OPVs can work well (Figure S1). The devices with c-TiO2 exhibited a lower average PCE (9.4%) than that of the devices with ZnO (10.1%) as a consequence of the
decreased short-circuit current density ($J_{SC}$) and fill factor (FF). Due to the high processing temperatures involved, all the OPV devices were fabricated on fluorine-doped tin oxide (FTO) substrates, but devices based on indium-doped tin oxide (ITO) substrates were also evaluated (Figures S2 and S3). The average and maximum performance values of the devices based on the ITO/ZnO structure are presented in Table S1. The average PCE of the ITO/ZnO devices was 10.0%, comparable with the FTO/ZnO devices. For the devices incorporating the mp-TiO$_2$, with increasing mp-TiO$_2$ thickness, the $J_{SC}$ and PCE increased to a maximum peak before subsequently decreasing with a continued increase in layer thickness (Table 1). The devices with mp-TiO$_2$ exhibited enhanced performance as compared with the devices with c-TiO$_2$ and ZnO. The average $J_{SC}$ increased from 17.7 to 18.4 to 20.1 mA cm$^{-2}$ for the c-TiO$_2$- and ZnO-based devices, respectively. The enhanced $J_{SC}$ may result from the light-manipulation effect of the rigid scaffold structure mp-TiO$_2$ layer. The average FF increased from 67.2% to 68.3% as compared with devices with c-TiO$_2$ and slightly decreased from 70.2% to 68.3% as compared with devices with ZnO. As a result, the mp-TiO$_2$-based devices exhibited a higher average PCE (10.6%) than that of the c-TiO$_2$-based (9.4%) and ZnO-based (10.1%) devices. The best PCE attained for a mp-TiO$_2$-based device was as high as 11.2%. As shown in Figure 2B, the trend observed in the EQE spectra was like the one seen for the $J_{SC}$. In the wavelength range between 450 and 750 nm, the observed high EQE values mainly came from the contribution of PffBT4T-C$_9$C$_{13}$, while the EQE peaks below 450 nm stemmed from the PC$_{71}$BM. Based on the EQE data, it can be argued that the overall EQE was enhanced by using the mesoporous structure. The calculated $J_{SC}$ values obtained from the integration of the EQE spectra with the AM 1.5G reference spectrum were close to the measured values (the average mismatch was 2.5%; Table 1).

After the thermal stability test, the average PCEs of the devices with ZnO as the ETL decayed from 10.1% to 4.7%, while the PCEs of the devices with c-TiO$_2$ as the ETL likewise fell from 9.4% to 4.3%. They retained only 47% and 44% of their original values, respectively, upon being subjected to the thermal stability test. On the other hand, the devices with the mp-TiO$_2$ as the ETL demonstrated an improved thermal stability. After the same thermal stability test, the average PCE of the mp-TiO$_2$-based devices decayed from 10.6% to 7.3%, preserving 69% of its original value. The corresponding average open-circuit voltage ($V_{OC}$), $J_{SC}$, and FF curves for the different ETLs as a function of the annealing time at 120°C are presented in Figure 3.
Figures S4–S6, respectively. To further prove the role of mesoporous ETL, we fabricate devices based on different D/A blend (PBDTTT-EFT:PC_{71}BM, PffBT4T-2OD:PC_{71}BM, and PffBT4T-C9C13:ITIC); the devices based on mp-TiO_2 exhibited better thermal stability, about 50% higher than that with ZnO and c-TiO_2 (Figures S7–S9).

To further investigate the charge collection and extraction efficiencies in c-TiO_2- and mp-TiO_2-based devices, we carried out corrected photocurrent measurements. According to the literature, the corrected photocurrent is defined as the device current under illumination as a function of voltage after subtraction of the corresponding dark current ($J_{\text{ph}} = J_{\text{light}} - J_{\text{dark}}$). If the effective applied voltage ($V_0$, where $V_0$ is the voltage at which the currents measured under illumination and in the dark are equal) is large enough, all carriers generated by light absorption in the active layer will be swept out, leading to a saturated current ($J_{\text{sat}}$). The ratio of $J_{\text{ph}}$ to $J_{\text{sat}}$ represents the product of the charge separation, transportation, and extraction efficiencies. Figure 4 shows the $J_{\text{ph}}/J_{\text{sat}}$ ratios for devices using c-TiO_2 and mp-TiO_2 over a range of biases ($V_0 - V$). The $J_{\text{ph}}/J_{\text{sat}}$ of the mp-TiO_2 device at low electric fields was much higher than that of the c-TiO_2 device, which was attributed to the enhanced charge extraction and collection efficiencies. The enhanced charge extraction and collection efficiencies were hypothesized to be caused by the increased interfacial surface area between the active layer and the ETL.

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The resultant effect on the film morphologies after being subjected to the thermal stability test was investigated by grazing incident X-ray diffraction (GIXD) measurement. As shown in Figure 5, before the thermal stability test, all the blend films based on ZnO, c-TiO_2, or mp-TiO_2 showed strong (100) lamellar peaks at $q = 0.3 \text{ Å}^{-1}$ along either the in-plane direction or the out-of-plane direction, which suggests that all the polymers exhibited a mixture of “edge-on” and “face-on” configurations. After the thermal stability test, the molecular packing behavior of the blend films based on both planar structures (ZnO and c-TiO_2) was switched from the preferred “edge-on” or “face-on” microstructure to an orientationally random microstructure. In contrast, the molecular packing of the blend film with mp-TiO_2 maintained its original preferred orientation. Furthermore, the average extent of phase separation can be roughly determined by the intensity of the 2D GIXD patterns from the low $q$ region ($q < 0.1 \text{ Å}^{-1}$). From this, the phase separation in the blend films based on ZnO, c-TiO_2, or mp-TiO_2 before and after heating at 120°C for 60 min can be

<table>
<thead>
<tr>
<th>Electron-Transporting Layer</th>
<th>Heating Time (min)</th>
<th>$V_{\text{OC}}$ (V)</th>
<th>$J_{\text{SC}}$ (mA cm$^{-2}$)</th>
<th>Calculated $J_{\text{SC}}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0</td>
<td>0.78 ± 0.01</td>
<td>18.4 ± 0.5</td>
<td>18.2</td>
<td>70.2 ± 0.3</td>
<td>10.1 ± 0.2</td>
</tr>
<tr>
<td>ZnO</td>
<td>60</td>
<td>0.71 ± 0.01</td>
<td>11.9 ± 0.4</td>
<td>11.4</td>
<td>56.0 ± 0.3</td>
<td>4.7 ± 0.2</td>
</tr>
<tr>
<td>c-TiO_2</td>
<td>0</td>
<td>0.79 ± 0.01</td>
<td>17.7 ± 0.4</td>
<td>17.4</td>
<td>67.2 ± 0.4</td>
<td>9.4 ± 0.4</td>
</tr>
<tr>
<td>c-TiO_2</td>
<td>60</td>
<td>0.73 ± 0.01</td>
<td>10.5 ± 0.4</td>
<td>10.4</td>
<td>56.7 ± 0.4</td>
<td>4.3 ± 0.4</td>
</tr>
<tr>
<td>mp-TiO_2 (150 nm)</td>
<td>0</td>
<td>0.77 ± 0.01</td>
<td>20.1 ± 0.3</td>
<td>19.7</td>
<td>68.3 ± 0.3</td>
<td>10.6 ± 0.4</td>
</tr>
<tr>
<td>mp-TiO_2 (150 nm)</td>
<td>60</td>
<td>0.75 ± 0.01</td>
<td>15.6 ± 0.5</td>
<td>15.2</td>
<td>62.4 ± 0.3</td>
<td>7.3 ± 0.2</td>
</tr>
<tr>
<td>mp-TiO_2 (100 nm)</td>
<td>0</td>
<td>0.77 ± 0.01</td>
<td>17.6 ± 0.3</td>
<td>16.9</td>
<td>64.0 ± 0.3</td>
<td>8.7 ± 0.2</td>
</tr>
<tr>
<td>mp-TiO_2 (200 nm)</td>
<td>0</td>
<td>0.77 ± 0.01</td>
<td>18.2 ± 0.4</td>
<td>17.8</td>
<td>67.3 ± 0.5</td>
<td>9.4 ± 0.4</td>
</tr>
<tr>
<td>mp-TiO_2 (250 nm)</td>
<td>0</td>
<td>0.77 ± 0.01</td>
<td>16.5 ± 0.4</td>
<td>15.8</td>
<td>63.1 ± 0.3</td>
<td>8.1 ± 0.3</td>
</tr>
</tbody>
</table>
monitored from Figure 5. It is worth noting that there were significant changes in phase separation for the blends based on ZnO and c-TiO2 after heating, while the extent of phase separation of the blend film with mp-TiO2 remained unchanged. This is likely caused by the mesoporous structure, which functioned as a rigid scaffold to suppress the reorganization and motion of the polymer when heated. Since the device performance and stability could be very sensitive to morphological factors related to the blend layer, such as molecular packing and phase separation,31,42 the effective suppression of heat-induced phase separation by using this mesoporous interface layer resulted in an improved thermal stability.

Conclusion

In conclusion, mesoporous-structured OPVs show higher efficiency and better stability than their planar-structured counterparts. On this note, relative to the traditional planar ETL, a mesoporous ETL exhibits an improved charge-extraction efficiency due to its increased interfacial surface-area contact with the layer. This was demonstrated in this work whereby the best PCE of an OPV device incorporating a mesoporous TiO2 ETL was enhanced by 11% or 8% in relation to devices using a compact ZnO or TiO2, respectively. More importantly, the mesoporous structure of the ETL can serve as a rigid scaffold to suppress excessive aggregation of PC71BM and retain the optimized molecular packing of the donors at elevated temperatures, thereby contributing to improved device stability. Our results demonstrate that a mesoporous-structured ETL can be an excellent candidate for OPVs to both enhance efficiency and improve stability simultaneously.

EXPERIMENTAL PROCEDURES

Unless stated otherwise, solvents and chemicals were obtained commercially and used without further purification. PFBT4T-C9C13 and PBDTTT-EFT were purchased from Cal-OS. PFBT4T-2OD, ITIC, and PC71BM were purchased from Solarmer. Titanium diisopropoxide bis(acetylacetonate), 1-butanol, titanium chloride, 1,8-diodooctane (DIO), chlorobenzene (CB), and o-dichlorobenzene (DCB) were obtained from Sigma-Aldrich. Mesoporous titanium dioxide (TiO2) paste (30NR-D) was obtained from Dyesol. Organic photovoltaic devices were fabricated with the following structures: FTO/compact titanium dioxide (c-TiO2)/with or without mesoporous titanium dioxide (mp-TiO2) or zinc oxide (ZnO)/active layer/molybdenum trioxide (MoO3)/silver (Ag) and ITO/ZnO/active layer/molybdenum trioxide (MoO3)/silver (Ag). The FTO and ITO glass were precleaned in an ultrasonic bath of acetone and isopropanol and treated in an ultraviolet-ozone chamber (Jelight, USA) for 15 min. A thin layer (ca. 30 nm) of ZnO sol-gel solution was spin coated onto the FTO/ITO glass and baked at 200°C for 60 min. A compact TiO2 layer with thickness of ca. 30 nm was deposited on the FTO substrate by repeated spin coating of 0.15 M 1-butanol solution of titanium disopropoxide bis(acetylacetonate) twice. Between
every coating process, the substrate was dried on a hot plate at 125°C for 5 min and finally annealed at 500°C for 10 min. An mp-TiO₂ layer was deposited on top of the c-TiO₂ layer by spin coating a diluted TiO₂ paste in 1-butanol (1:6 [v/v]) for 30 s. The film was annealed at 500°C for 1 h. After cooling down to room temperature, the film was exposed to ultraviolet ozone for 15 min before being treated with 20 mM aqueous TiCl₄ solution at 70°C for 10 min. The TiCl₄-treated film was cleaned with deionized water and annealed again at 500°C for 30 min. A mixture of PFBT4T-C₉C₁₃:PC₇₁BM was dissolved in DCB/CB/DIO (50:50:1.5 [v/v/v]) mix solvent (D/A = 1:1.2, 17.6 mg mL⁻¹ in total) with stirring for at least 1 h (110°C). This blend solution was then spin coated on the preheated (110°C) ZnO or TiO₂ substrates to form the active layer. The thickness of the active layer was ca. 250–350 nm. For the PBDTTT-EFT:PC₇₁BM-based devices, a mixture of PBDTTT-EFT:PC₇₁BM was dissolved in CB/DIO (100:3 [v/v]) mix solvent (D/A = 1:1.5, 45 mg mL⁻¹ in total) with stirring overnight (60°C). This blend solution was then spin coated on the preheated (100°C) ZnO or TiO₂ substrates to form the active layer. The thickness of the active layer was ca. 250–350 nm. For the PFBT4T-2OD:PC₇₁BM-based devices, a mixture of PFBT4T-2OD:PC₇₁BM was dissolved in CB/DCB/DIO (50:50:2.5 [v/v/v]) mix solvent (D/A = 1:1.2, 17.6 mg mL⁻¹ in total) with stirring for at least 1 h (100°C). This blend solution was then spin coated on the preheated (100°C) ZnO or TiO₂ substrates to form the
active layer. The thickness of the active layer was ca. 250–350 nm. For the PffBT4T-C9C13:ITIC-based devices, a mixture of PffBT4T-C9C13:ITIC was dissolved in CB/DCB/DIO (50:50:1 [v/v/v]) mix solvent (D/A = 1:1.5, 25 mg mL\(^{-1}\) in total) with stirring for at least 1 h (100°C). This blend solution was then spin coated on the preheated (100°C) ZnO or TiO\(_2\) substrates to form the active layer. The thickness of the active layer was ca. 250–350 nm. After finishing the previous steps, a MoO\(_3\) (ca. 10 nm) and Ag (ca. 100 nm) layer was then evaporated onto the surface of the photosensitive layer under vacuum (ca. 10\(^{-5}\) Pa) to form the back electrode. The active area of the device was determined by the aperture, which was 0.1 cm\(^2\). 

J-V characteristics of the photovoltaic cells were measured using a Keithley 2400 source measure unit under a simulated AM 1.5G spectrum with an Oriel 9600 solar simulator. EQEs were measured by an integrated system (Enlitech, Taiwan) and a lock-in amplifier with a current preamplifier under short-circuits’ condition. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The thermal stability test of solar cells was carried out under continuous heating at 120°C for 1 h, and the J-V was measured under a simulated AM 1.5G spectrum with an Oriel 9600 solar simulator. These tests were carried out in a nitrogen-filled glovebox.

GIXD measurement was performed at the Advanced Light Source on the 7.3.3 beamline. All samples were deposited on a silicon wafer with 100-nm silicon oxide according to the same procedure as with the device fabrication. Samples were irradiated by 10 keV at a fixed X-ray incident angle of 0.14° with an exposure time of 10 s. The scattering pattern was collected by a 2D detector. The film thickness was measured by a Veeco Dektak 150. The UV-visible absorption spectra were measured with a U-4100 Hitachi with specified accessory. AFM images were taken with a Bruker Dimension FastScan Scanning Probe Microscope. SEM images were obtained by an FEI Nova NanoSEM 230.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.matt.2019.03.006.

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AUTHOR CONTRIBUTIONS
Y.Y. and R.W. conceived the idea. R.W. performed the device fabrication and data analysis. S.-Y.C., L.M., W.H., J.-W.L., and P.S. assisted with the device characterization. H.-Y.C., T.H., Y.L., and J.X. assisted with the data analysis and device fabrication. C.Z. carried out the GIXD measurement. R.W. and P.C. wrote the manuscript. P.C. provided helpful discussions during the project. All the authors discussed the results and commented on the manuscript. Y.Y. supervised the project.

DECLARATION OF INTERESTS
The authors declare no competing interests.
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