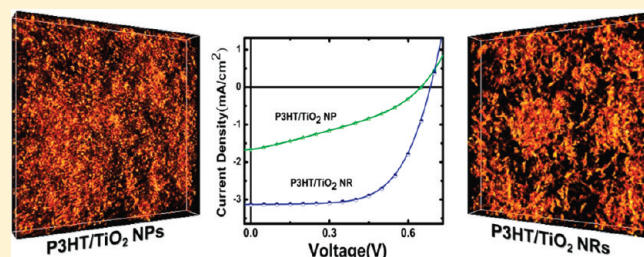


Interplay of Three-Dimensional Morphologies and Photocarrier Dynamics of Polymer/TiO₂ Bulk Heterojunction Solar CellsShao-Sian Li,^{†,⊥} Ching-Pin Chang,^{†,‡,⊥} Chih-Cheng Lin,[†] Yun-Yue Lin,[†] Chia-Hao Chang,[†] Jer-Ren Yang,[†] Ming-Wen Chu,[‡] and Chun-Wei Chen^{*,†}[†]Department of Materials Science and Engineering and [‡]Center for Condensed Matter Sciences, National Taiwan University, Taipei, 106, Taiwan

S Supporting Information W Web-Enhanced

ABSTRACT: In this study, we investigated the interplay of three-dimensional morphologies and the photocarrier dynamics of polymer/inorganic nanocrystal hybrid photoactive layers consisting of TiO₂ nanoparticles and nanorods. Electron tomography based on scanning transmission electron microscopy using high-angle annular dark-field imaging was performed to analyze the morphological organization of TiO₂ nanocrystals in poly(3-hexylthiophene) (P3HT) in optimal solar cell devices. The Three-dimensional (3D) morphologies of these hybrid films were correlated with the photocarrier dynamics of charge separation, transport, and recombination, which were comprehensively probed by various transient techniques. Visualization of these 3D bulk heterojunction morphologies clearly reveals that elongated and anisotropic TiO₂ nanorods in P3HT not only can significantly reduce the probability of the interparticle hopping transport of electrons by providing better connectivity with respect to the TiO₂ nanoparticles, but also tend to form a large-scale donor–acceptor phase-separated morphology, which was found to enhance hole transport. The results support the establishment of a favorable morphology for polymer/inorganic hybrid solar cells due to the presence of the dimensionality of TiO₂ nanocrystals as a result of more effective mobile carrier generation and more efficient and balanced transport of carriers.



In the past decade, polymer solar cells have attracted great interest in the development of low-cost, large-area, and mechanically flexible photovoltaic devices.^{1–3} Due to the short exciton diffusion length (~ 10 nm) of a semiconducting polymer,⁴ the electron acceptors are usually intermixed with polymers (electron donors) at a nanometer length scale to form bulk heterojunctions (BHJs). Extensive research has focused on the development of polymer photovoltaic devices using fullerene or fullerene derivatives as acceptors, and recent advances have achieved high photovoltaic efficiencies in excess of 7%.⁵ An alternative type of acceptor in polymer solar cells is based on inorganic semiconductor nanocrystals, taking advantage of their relatively high electron mobility and good physical and chemical stability. Various inorganic nanocrystals such as CdSe,^{3,6} TiO₂,⁷ PbS,⁸ and ZnO⁹ have been used in polymer/inorganic hybrid BHJ solar cells. In the class of inorganic acceptors, metal oxide nanocrystals such as TiO₂ and ZnO are two of the most promising materials since they are environmentally friendly and low-cost. Polymer solar cells based on various nanoscale morphologies of nanocrystal metal oxides, ranging from well-dispersed nanoparticles or nanorods^{7,9} to well-connected nanoporous or aligned nanorod structures grown directly on substrates,^{10–12} have been reported. Until now, the best polymer/metal oxide hybrid solar cells have been based on the BHJ architecture, blending dispersed nanocrystals within polymers. However, due to the strong incompatibility between inorganic

nanocrystals and polymers, the precarious control of the BHJ morphology of the two intermixed components becomes more challenging than with the conventional polymer/fullerene hybrid solar cells. To overcome this drawback, Janssen et al. used the method of *in situ* generation of the inorganic semiconductor inside the organic material to control the morphology of poly(3-hexylthiophene) (P3HT)/ZnO nanoparticle hybrids, giving a best power conversion efficiency of 2.0%.⁹ By contrast, we have recently demonstrated a power conversion efficiency of 2.2% for polymer solar cells based on P3HT/TiO₂ nanorod BHJs through an interface modification between P3HT and TiO₂ nanorods, and these hybrid films were deposited from the solution in a single step, similar to the common deposition methods.⁷ In addition to the improvement of organic/inorganic interfaces, the nanocrystal shape is another parameter affecting the performance of polymer/inorganic hybrid solar cells.^{13,14} The morphological organization of differently shaped nanocrystals within a polymer matrix strongly affects the photocarrier dynamics of the active layers and thus the photovoltaic performance. Recently, three-dimensional (3D) electron tomography has become an ideal tool for gaining insight into the nanoscale organization of BHJ polymer solar cells, providing the critical morphological parameters for improving the device performance.^{9,13,15,16} Here,

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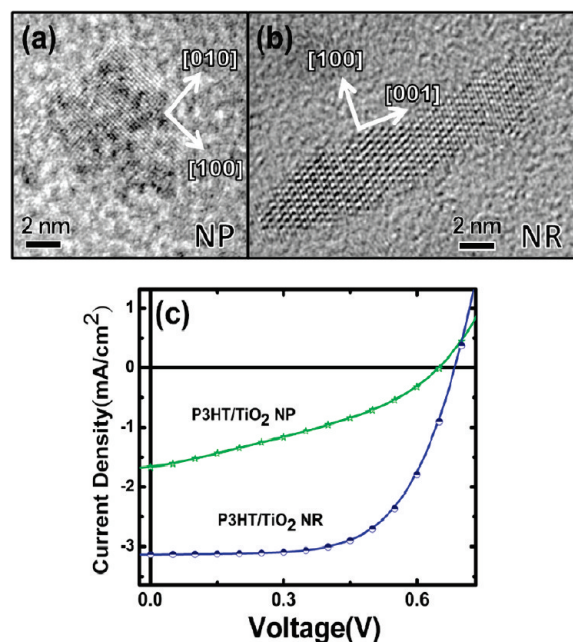


Figure 1. High-resolution TEM image of TiO₂ (a) NPs and (b) NRs. (c) Current–voltage characteristics of P3HT/TiO₂ NP (green) and NR (blue) hybrid solar cell devices.

we employed electron tomography based on scanning transmission electron microscopy using high-angle annular dark-field (STEM-HAADF) imaging to probe the 3D morphological organization of P3HT/TiO₂ hybrid BHJs with different nanocrystal shapes, including nanoparticles (NPs) and nanorods (NRs). We also performed a comprehensive analysis of the photocarrier dynamics corresponding to the 3D structures of these blends, including charge separation, transport, and recombination as probed by various transient techniques including time-resolved photoluminescence (TRPL) spectroscopy, transient open-circuit voltage decay (TOCVD) measurements, time-of-flight (TOF) techniques, and photo-assisted charge extraction with a linearly increasing voltage (photo-CELIV) measurements. The interplay between the nanocrystal shape-dependent 3D morphology and the photocarrier dynamics enables us to understand the key factors to further improve the device performance of polymer/inorganic hybrid solar cells.

The growth of the anatase TiO₂ NPs and NRs that were synthesized is described in the Supporting Information (SI). Figure 1a,b shows high-resolution transmission electron microscopy (HRTEM) images of the TiO₂ nanocrystals with a characteristic size of ~ 5 nm for the NPs and ~ 4 nm (diameter) $\times$ ~ 20 nm (length) for the NRs, respectively. The as-synthesized TiO₂ NPs and NRs are usually capped with an insulating surfactant of oleic acid (OA), consisting of a long alkyl chain, which acts as a potential barrier for the charge transfer. In this study, we used ligand exchange treatment by pyridine on both TiO₂ NPs and NRs to remove the original OA surfactant to improve the device performances.⁷ We fabricated the photovoltaic devices by spin-coating the photoactive layers, which consisted of P3HT/TiO₂ NP and NR hybrids on top of the ITO/PEDOT:PSS anode electrode. The Al electrode was then deposited onto the active layer by thermal evaporation. Various weight ratios of P3HT to TiO₂ nanocrystals were tested under similar conditions, and the optimal device performance for both

P3HT/TiO₂ NP and NR hybrid thin films could be obtained with a 50:50 (wt %) ratio. The morphology of the P3HT/TiO₂ hybrid thin films became poor when the concentration of TiO₂ NPs or NRs was larger than 70 wt %, when a large aggregation of nanocrystals can be observed using the optical microscope. Figure 1c shows the current–voltage characteristics of photovoltaic devices under a simulated A.M. 1.5 illumination (100 mW/cm^2). The device based on the P3HT/TiO₂ NP hybrid thin film exhibits a short-circuit current density (J_{sc}) of 1.65 mA/cm^2 , an open-circuit voltage (V_{oc}) of 0.60 V , and a fill factor (FF) of 0.42 , resulting in a power conversion efficiency (η) of 0.42% . By contrast, the P3HT/TiO₂ NR hybrid device shows a largely improved photovoltaic performance, with $J_{sc} = 3.10 \text{ mA/cm}^2$, $V_{oc} = 0.69 \text{ V}$, and $FF = 0.62$, giving $\eta = 1.33 \%$. The better-performing P3HT/TiO₂ NR hybrid device compared to its NP counterpart indicates that nanocrystal shape can largely affect device performance. In particular, the relatively high $FF = 0.62$ of the P3HT/TiO₂ NR hybrid device suggests that a favorable BHJ morphology may exist for efficient carrier transport or collection. Understanding how the organization of these differently shaped nanocrystals within the polymer affects the corresponding photocarrier dynamics and the photovoltaic performance of the P3HT/TiO₂ hybrid solar cells is of great interest.

Next, we performed STEM-HAADF electron tomography to reveal the 3D morphologies of TiO₂ NPs and NRs in P3HT. For a BHJ solar cell, the formation of a nanoscale bicontinuous donor–acceptor network is crucial to obtain efficient photovoltaic performance.¹⁷ Therefore, determining the exact 3D features of the embedded donor and acceptor materials is of vital importance. Electron tomography, with its unparalleled nanometer-scale resolution in 3D imaging, is an indispensable technique for unraveling this problem. Visualization of the 3D transport pathways for holes or electrons has been recently demonstrated in various types of hybrid solar cells using TEM tomography.^{9,16} However, the focus-dependent phase/diffraction contrasts inherent to TEM imaging are susceptible to artifact creations in the associated 3D reconstructed volumes.^{15,18,19} Regarding this aspect, STEM-HAADF imaging represents an optimal solution because the corresponding contrast is purely incoherent and arises from thermal diffused scattering, which is ultimately amplitude contrast (sensitive to atomic numbers only) and is robust to electro-optical focusing conditions, unlike TEM.^{13,18–20} The interpretation of images in STEM-HAADF is thus straightforward, with the dark (bright) contrasts attributed to light (heavy) matter, that is, P3HT for the dark contrasts and TiO₂ for the bright ones in our current case. Figure 2a,b shows snapshots of the 3D reconstructed grayscale images of P3HT/TiO₂ NP and NR hybrid thin films, respectively. The two reconstructed images show very different nanoscale morphologies of TiO₂ nanocrystals distributed in P3HT. The intermixing between TiO₂ NPs and P3HT is found to be more significant than in the P3HT/TiO₂ NR hybrid. By contrast, a larger scale of phase separation, consisting of several more distinct TiO₂ NR-rich clusters separated by P3HT domains, can be clearly observed in the P3HT/TiO₂ NR hybrid thin film. Figures 2c,d further exhibits these tomography images viewed from different angles. Because the photogenerated carriers are expected to be transported through the films and collected at the top and bottom electrodes, the morphological organization of TiO₂ nanocrystals along the direction perpendicular to the substrate is the most important when determining the photovoltaic performance. We have further sliced the reconstructed volumes to gain insight into

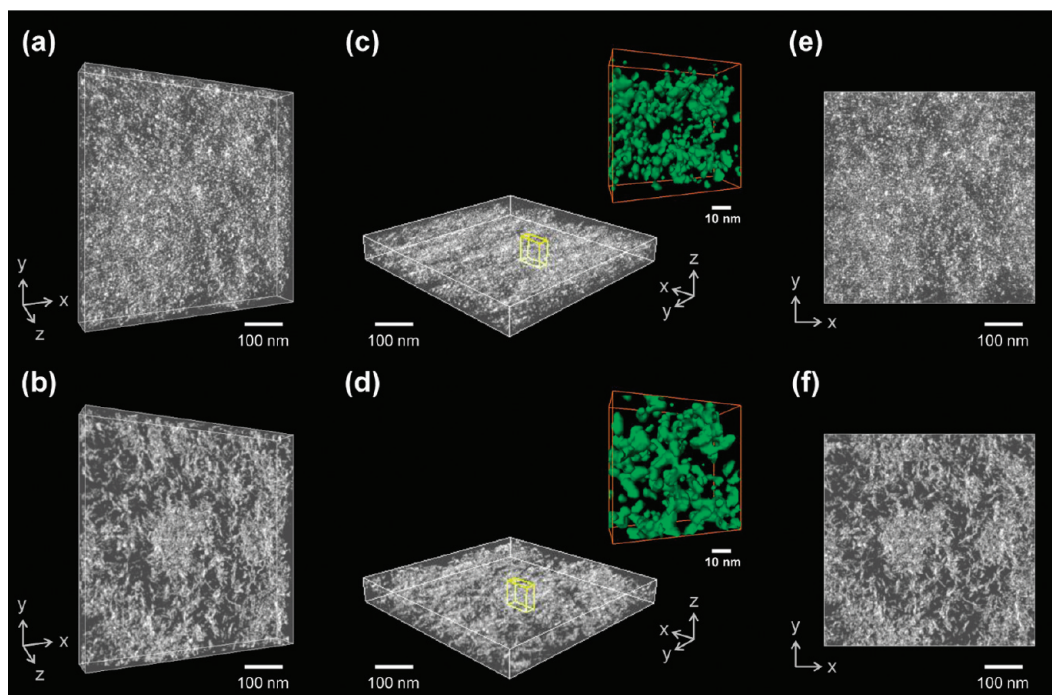


Figure 2. STEM-HAADF electron tomography images of the P3HT/TiO₂ NP (a,c) and NR (b,d) hybrid thin films viewed from different angles. The dimension of these films is about 570 nm × 570 nm × 70 nm. The insets in (c) and (d) show the connective networks along the film direction formed by TiO₂ NPs and NRs. The size of these two slices is about 70 nm × 30 nm × 70 nm. (e,f) 2D projection images of the respective 3D view-graphs in (a) and (b) along the film thickness direction. Video files of all the reconstructed volumes and slices lying in the horizontal planes of the NP (movie 1) and NR (movie 2) hybrid films are available in the online (HTML) version of this article.

the information of the connective networks along the vertical direction formed by TiO₂ NPs and NRs, as shown in the insets of Figure 2c,d, conducted by the surface rendering method with the contrast threshold set to remove the low-background contrast resulting from the P3HT matrix. It is clearly seen that the anisotropic TiO₂ NRs can largely reduce the number of junctions of a connective network compared to the TiO₂ NPs, which are isotropic without any preferred orientation. The aspect ratio of the TiO₂ NRs with preferred orientations angled toward the plane of the film provides a better chance for them to form a connective network between two electrodes. This has the advantage of reducing the probability of interparticle hopping and facilitating carrier transport. Figure 2e,f further exhibits two-dimensional projection images of the respective 3D view-graphs along the film thickness direction, where a larger amount of phase-separated TiO₂ NR-rich domains surrounded by P3HT can be clearly observed. The corresponding video files of all the rotating 3D reconstructed volumes and slices lying in the horizontal planes of the P3HT/TiO₂ NP and NR hybrid films are available in the online (HTML) version of this article. It is noted that the optimal morphology of the P3HT/TiO₂ NR hybrid solar cell is very different from that of another widely studied polymer/inorganic hybrid solar cell using CdSe NRs, where a much higher concentration of CdSe NRs was used due to their contribution to light harvesting.^{13,14} In addition, it is also found that the dispersion of TiO₂ nanocrystals in our system is less homogeneous as compared to the optimal morphology in the P3HT/ZnO NP hybrid solar cells using the method based on *in situ* generation of the inorganic nanocrystals inside the organic material to reduce aggregation.⁹ Therefore, the above tomography analyses clearly reveal two pieces of important 3D morphological

information about P3HT/TiO₂ BHJs: (i) the presence of dimensionality of the TiO₂ nanocrystals in P3HT enables the formation of an interconnecting network that can provide better connectivity due to the anisotropy, and (ii) the P3HT/TiO₂ NR hybrid is favored to form large-scale donor–acceptor separated phases compared to its NP counterpart. The significantly improved performance of the P3HT/TiO₂ NR hybrid device over its NP hybrid counterpart may be qualitatively attributed to the establishment of a favorable 3D morphology that more closely resembles the ideal bicontinuous donor–acceptor phase-separated morphology of typical high-performance polymer solar cells.

To further quantitatively correlate the nanocrystal-shape dependent morphology to the photovoltaic performance, we carried out a series of transient measurements to investigate the photocarrier dynamics of these P3HT/TiO₂ nanocrystal BHJ hybrid films. The performance of polymer photovoltaic devices is known to be largely influenced by the mechanisms of charge separation, transport, and recombination, which are strongly dependent on the film morphology. The charge separation of a polymer is usually a two-step process where excitons are first separated to less strongly bound electron–hole pairs and finally to free carriers.²¹ We performed TRPL spectroscopy to examine the exciton dissociation efficiency in the P3HT/TiO₂ NP and NR hybrid thin films, as shown in Figure 3a. The addition of TiO₂ nanocrystals in polymer usually resulted in a new relaxation process, which provided the donor (P3HT) with a further nonradiative process and led to quenching of PL emission and shortening of the measured lifetime τ_{PL} . The PL was largely quenched after TiO₂ nanocrystals were added to P3HT (inset), which was accompanied with a much shorter PL decay time. The decay time for the pristine P3HT is 650 ps. The P3HT/TiO₂ NP

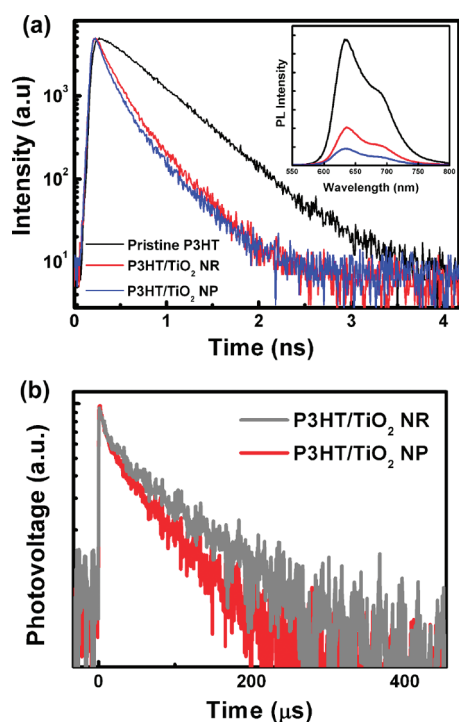


Figure 3. (a) TRPL spectroscopy of pristine P3HT and P3HT/TiO₂ NR and NP hybrids. The inset shows the PL intensities of these samples. (b) Transient photovoltage decay curves of the P3HT/TiO₂ NR and NP hybrid solar cell devices in the TOCVD measurement.

hybrid had a lower yield of PL emission (inset) and a shorter PL decay lifetime of 232 ps, compared to 251 ps in the P3HT/TiO₂ NR hybrid, indicating more efficient exciton dissociation. The morphology data showed that a large number of interfaces between P3HT and TiO₂ NPs existed due to the higher intermixing compared to that in the P3HT/TiO₂ NR hybrid. The average distance of an exciton generated in a polymer diffusing to the heterojunctions is expected to be shorter as a result of more efficient exciton dissociation in the P3HT/TiO₂ NP hybrid than in the NR counterpart. After exciton dissociation, electrons and holes either recombined at the P3HT/TiO₂ interfaces or became free carriers to be transported through the conducting paths formed by the TiO₂ nanocrystals and P3HT, respectively. Next, we performed the TOCVD measurement to determine the recombination rate at the interfaces of the P3HT and TiO₂ nanocrystals using the operating photovoltaic devices. In the TOCVD measurement, the devices operated at the open-circuit condition (V_{oc}) under the white light bias source. Since no charge was collected at the V_{oc} condition, a small perturbation generated by a pulsed laser was used to generate extra electrons and holes in hybrids. The extra electrons and holes recombined at the P3HT/TiO₂ nanocrystals interfaces with a lifetime τ_{rec} resulting in the decay of the transient photovoltage. Figure 3b shows the photovoltage decay curves of the devices based on the P3HT/TiO₂ NR and NP hybrids. The P3HT/TiO₂ NR hybrid device shows a slower recombination rate at the interfaces with a longer $\tau_{rec} = 77.4 \mu s$, compared to the P3HT/TiO₂ NP hybrid device with $\tau_{rec} = 54.3 \mu s$. In a previous study, we showed that the interfacial ligand molecules on the TiO₂ nanocrystal surface can significantly affect the recombination rates at the P3HT/TiO₂ interfaces. Although the same interface modification treatment

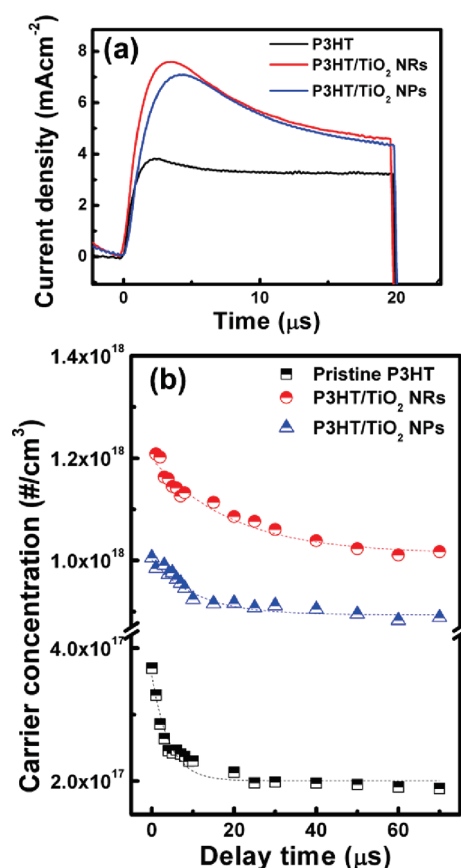


Figure 4. (a) Typical photo-CELIV transient curves derived from P3HT and P3HT/TiO₂ NR and NP hybrid devices. (b) Carrier concentrations of these devices derived from different delay times with exponentially fitting curves.

was performed in both TiO₂ NPs and NRs in this study, the lower recombination rate for the P3HT/TiO₂ NR hybrid device can be mainly attributed to (i) the overall smaller interface area between the P3HT and TiO₂ NRs compared to the P3HT/TiO₂ NP hybrid, which may reduce the recombination probability in the surface states or traps,²² or (ii) more effective distancing of the electrons and holes from the dissociation sites after charge separation, even in the absence of an internal electric field, as a result of the establishment of a more favorable morphology of the optimal P3HT/TiO₂ NR hybrid device.

Once these photogenerated carriers are separated as free electrons and holes, they either have to be transported to their respective electrodes by the built-in electric field of the device or undergo recombination. The holes are expected to be transported through the P3HT chains and the electrons along the TiO₂ nanocrystals. We therefore carried out the photo-CELIV measurement and TOF measurement to determine the carrier concentration, recombination lifetime, and mobility of the hybrid films. The photo-CELIV technique simultaneously enables the determination of the mobility and recombination rate of free carriers in real photovoltaic devices. It employs a pulsed laser to excite photogenerated carriers inside the active material, followed by an extraction of the free carriers using a triangular voltage ramp with a reverse bias and a controlled delay time.^{23–25} The typical transient curves of the pristine P3HT, P3HT/TiO₂ NR, and P3HT/TiO₂ NP devices are shown in Figure 4a. The

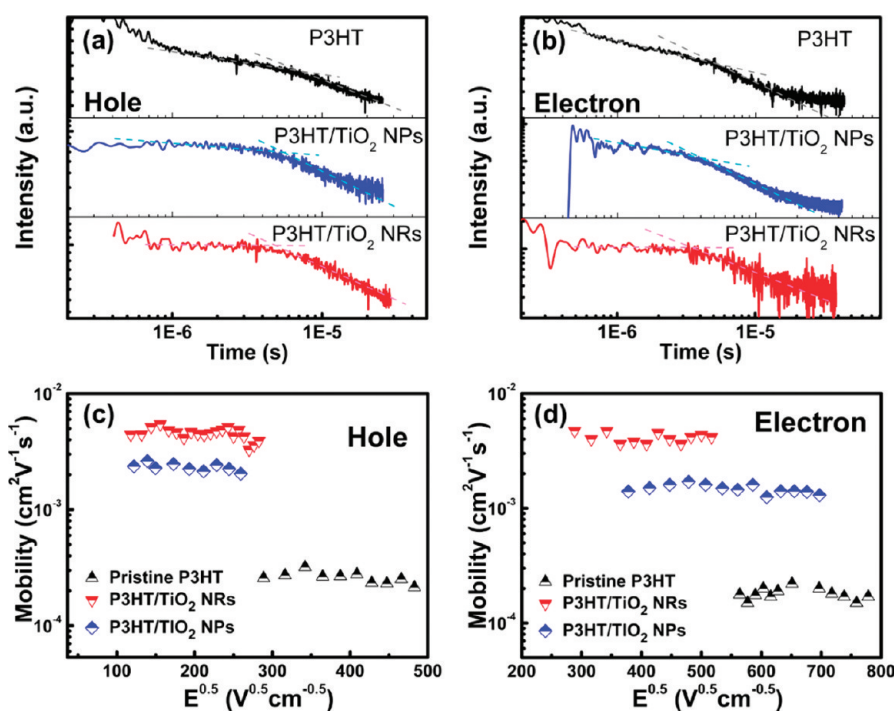


Figure 5. Typical double-logarithmic plots of TOF transient photocurrent for (a) hole and (b) electron transport. The transit time t_{tr} can be estimated from the intersection point in the double-logarithmic plot. Field-dependent mobilities of (c) hole and (d) electron of P3HT and P3HT/TiO₂ NR and NP hybrid films.

variations in charge carrier concentrations of these devices are derived from the different delay times that can be estimated by integrating the conduction current over the extraction time according to eq (1) in the SI.²⁵ The P3HT/TiO₂ NR BHJ device exhibits higher carrier concentrations than the NP counterpart at all delay times. Although the initial photogenerated exciton dissociation in the P3HT/TiO₂ NP hybrid is more efficient, the establishment of a favorable morphology in the P3HT/TiO₂ NR hybrid enables the overall generation of mobile carriers to be transported toward electrodes more effectively, giving a higher carrier concentration. By fitting the concentration decay curve in Figure 4b, we are able to estimate the carrier recombination lifetime τ_R . The P3HT/TiO₂ NR hybrid device exhibits a longer $\tau_R = 23.5 \mu\text{s}$, compared to the P3HT/TiO₂ NP counterpart with $\tau_R = 10.9 \mu\text{s}$, indicating that a more efficient carrier transport and collection occurred. A very short $\tau_R = 4.13 \mu\text{s}$ was also observed in the pristine P3HT device, indicating that electrons and holes significantly recombined during the transport due to the lack of well-separated hole and electron transport paths. The prolonged recombination lifetime in the P3HT/TiO₂ NR hybrid device is also reflected in the enhanced carrier mobility as estimated from the transient curves according to eq (2) in the SI.^{23,24} Because electrons and holes cannot be individually extracted by photo-CELIV measurement, the calculated mobility is mainly attributed to the contribution of two types of carriers. An effective mobility of about $9.1 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ (delay time = $10 \mu\text{s}$) was obtained from the P3HT/TiO₂ NR hybrid device, which is nearly 3 times that of the NP counterpart ($\sim 3.1 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$, delay time = $10 \mu\text{s}$).

To further differentiate the effect of the 3D morphology on the efficiency of electron and hole transport, we performed the TOF technique, which is well-established for measuring charge mobility in organic thin films, to extract the unipolar carrier mobility of

the electrons or holes. Figure 5a,b shows the typical hole and electron transient curves of pristine P3HT and P3HT/TiO₂ NR and NP hybrid thin films, respectively. The hole and electron transient photocurrent for the pristine P3HT is highly dispersive, and the typical transit time t_{tr} of the carriers can be estimated from the intersection point in the double-logarithmic plot. In contrast, the corresponding hole and electron transient photocurrent for the P3HT/TiO₂ NR and NP hybrids is less dispersive, with a more clearly defined plateau region. Figure 5c,d shows hole and electron mobilities μ of these thin films at different applied electric fields by plotting $\log \mu$ versus the square root of the electric field ($\sqrt{E}$) in the Poole–Frenkel form.²⁶ All the samples show a very weak field dependence on the mobilities of electrons and holes. For the pristine P3HT sample, ambipolar transport with electron and hole mobilities in the range of $(1-2) \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ were obtained, similar to the results reported in the literature.²⁷ The significantly increased electron mobility after addition of TiO₂ NRs or NPs to P3HT is mainly due to the formation of electron conductive pathways by TiO₂ nanocrystals. The electron mobility of the P3HT/TiO₂ NR hybrid is about $4.5 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ higher than the $1.2 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ of the P3HT/TiO₂ NP hybrid due to the formation of more effective conducting networks with a reduced number of interparticle hopping and a less dispersive electron transport. Most interestingly, the addition of TiO₂ NPs or NRs to P3HT also causes a large enhancement in hole mobility of the hybrid films, with less dispersive transport in comparison to the pristine P3HT. Since TiO₂ nanocrystals usually demonstrate very effective hole-blocking, the transport of holes in TiO₂ NRs or NPs in the hybrid films is unlikely.^{28,29} In addition, it was demonstrated that the hole mobility of P3HT was enhanced by infiltration into the insulating nanopores,³⁰ which enables holes to be transported within the confined P3HT nanodomains.

Table 1. Summary of All the Photocarrier Dynamics Measured in This study by TRPL Spectroscopy, TOCVD Measurement, Photo-CELIV Measurement, and TOF Technique

	P3HT	P3HT/TiO ₂ NP	P3HT/TiO ₂ NR
exciton lifetime by TRPL (ps)	650	232	251
recombination lifetime by TOCVD (μ s)	—	54.3	77.4
carrier transport lifetime by photo-CELIV (μ s)	4.13	10.9	23.5
carrier mobility by TOF ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^a			
hole	2.5×10^{-4}	2.2×10^{-3}	4.6×10^{-3}
electron	2.0×10^{-4}	1.2×10^{-3}	4.5×10^{-3}

^aThe TOF hole (electron) mobilities for P3HT and P3HT/TiO₂ NP and NR hybrid films were measured at electric fields of 1.6×10^5 (3.6×10^5), 4.0×10^4 (2.0×10^5), and 4.0×10^4 (2.0×10^5) V/cm, respectively.

Therefore, the change of P3HT morphology after addition of TiO₂ nanocrystals may be responsible for the increased hole mobility of the hybrid films. As observed from the above tomography images, the establishment of separate P3HT and TiO₂ nanocrystal transport pathways allows holes to move through the P3HT domains surrounded by the TiO₂ nanocrystals to reduce recombination and facilitate transport. Therefore, the P3HT/TiO₂ NR hybrid film that consists of more distinct donor–acceptor phases along the direction perpendicular to the substrate exhibits a higher hole mobility, around $4.6 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$, than the P3HT/TiO₂ NP hybrid, with a mobility of $2.2 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$. Although it should be noted that there might be some deviation of the absolute mobility values of the thin photovoltaic devices compared with the thicker TOF samples, the establishment of an optimal morphology comprising an elongated and anisotropic TiO₂ NR within the P3HT enables more efficient and balanced transport of both electrons and holes, which may account for the higher values of FF, J_{sc} , and η . Table 1 summarizes all the photocarrier dynamics results obtained in this study.

This work demonstrated the interplay between the 3D morphological organization of P3HT/TiO₂ nanocrystal hybrid solar cells and the corresponding photocarrier dynamics and photovoltaic performance. The presence of dimensionality of nanocrystals and the more distinct donor–acceptor separated phases in the P3HT/TiO₂ NR hybrids represents a favorable morphology for high-performance polymer solar cells, having more effective carrier generation, transport, and collection. Further improvements in device performance can be achieved by optimizing the sizes and shapes of the TiO₂ nanocrystals or aligning them to enhance carrier transport.

■ ASSOCIATED CONTENT

S Supporting Information. Description of the synthesis of materials, device fabrication, and materials characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

W Web Enhanced Feature. Video files containing of all the rotating 3D reconstructed volumes and slices lying in the horizontal planes of the hybrid films are included in the online (HTML) version of this article.

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Interplay of Three-Dimensional Morphologies and Photocarrier Dynamics of Polymer/TiO₂ Bulk Heterojunction Solar Cells

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Experimental section:

Preparation of Materials:

Synthesis of TiO₂ nanoparticles & nanorods: Anatase TiO₂ nanorods were obtained according to the literature with modification.⁷ In brief, oleic acid (O.A., 90%, ACROS) was degassed at 120 °C for 1 h under vigorous stirring in a flask, after which it was cooled to 90 °C under nitrogen flow. Titanium (IV) isopropoxide (TTIP, 98%, ACROS) was then added and allowed to stir for 5 min. The resulting solution turned from colorless to pale yellow, indicating the formation of the complex. An

aqueous base solution of trimethylamine-N-oxide (TMAO, 98%, ACROS) was loaded into a syringe and then rapidly injected and kept at 90°C for 9 hours for proceeding hydrolysis and crystallization. Synthesis of TiO₂ nanoparticles was identical with the above procedures. Ethyleneglycol dissolved TMAO was injected into the mixed solution of degassed O.A. and TTIP to slow down the hydrolysis rate of TTIP. The resulting TiO₂ nanoparticle solution was heated at 90 °C for two days for crystallization. The TiO₂ nanocrystals (nanorods and nanoparticles) were purified by precipitated processes. The resulting solution of TiO₂ nanocrystals were precipitated upon addition of an excess of ethanol to the reaction mixture at room temperature. The resulting precipitates were isolated by centrifugation and washed several times with ethanol to remove the surfactant residual to obtain the TiO₂ nanocrystals.

Ligand exchange of TiO₂ nanocrystals: TiO₂ nanocrystals were precipitated by ethanol. The precipitant was then re-dispersed in pyridine (20ml, 99%, ACROS), and the resulting solution was under strong sonication for homogeneous dispersion of TiO₂ nanocrystals. The TiO₂ nanocrystals/pyridine solution was then allowed to keep at 75 °C till the solution turned clear. Accordingly, the original ligand molecules of O.A. were removed and the pyridine molecules of a weak bonded ligand that were on the surface of the TiO₂ nanorods could be removed by heating.⁷ The hybrid materials were then prepared by adding various amounts of TiO₂ nanocrystals into P3HT(Mw~35000, PDI 1.62, RR 96%) solution in mixed solvent consisting of pyridine, chloroform, and dichloromethane, and chlorobenzene to form P3HT/TiO₂ hybrid solutions.

Device fabrication and Materials Characterization:

Device fabrication and measurement: For the photovoltaic device fabrication, a 40 nm thick layer of PEDOT: PSS (Baytron P 4083) was spin-cast onto the pre-cleaned ITO substrate, followed by baking at 120°C for 30 minutes, then were moved into a nitrogen-purged glove box for subsequent depositions. The P3HT/TiO₂ hybrid solution was spin-cast onto PEDOT:PSS deposited substrate to form the active layer with a thickness of about 100 nm. The Al electrode was deposited by thermal evaporation in vacuum at a pressure around 2×10^{-6} torr. Current-voltage characteristics (Keithley 2410 source meter) were obtained by using a solar simulator (Newport Inc.) with an A.M.1.5 filter under irradiation intensity of 100mW/cm². An UV filter with a cutoff at 400 nm was used to avoid the optical excitation of TiO₂.

STEM-HAADF electron tomography: The free-standing specimens for electron tomography were prepared by etching the bottom PEDOT:PSS film as a sacrificial layer with water. The resulting hybrid thin films were floated onto the water surface and immediately transferred to the Cu grid for further STEM characterizations. STEM tomography experiments were conducted on a field-emission microscope operated at 200 keV (FEI F20 G²) with an electron-probe size of ~ 2 Å. Throughout the electron tomography investigations, no Bragg reflections were observed over the HAADF collection angles. The tilt series for each tomography study consists of 117 STEM-HAADF images, which were acquired from the tilting angles of -65° to 65°. The three-dimensional (3D) reconstructions of these two-dimensional (2D) STEM-HAADF datasets were performed using weighted back projection algorithm integrated in the FEI Inspect3D software package and further 3D visualization artworks were conducted using AMIRA 4.0 (Mercury Computer Systems).

Photocarrier dynamics measurements: For all the transient experiments, the devices were mounted in a vacuum chamber under 10^{-3} torr during measurement. TRPL spectroscopy was performed with a time-correlated single photon counting (TCSPC) spectrometer (Picoquant, Inc.). A pulse laser (470 nm) with an average power of 1 mW operating at 40 MHz with duration of 70 ps was used for excitation. In both TOCVD and Photo-CELIV measurements, the working solar cell devices were used. Measurements of TOCVD of the devices were made under open circuit conditions under illumination of adjustable intensity from a solar simulator. A small perturbation generated by a pulsed laser of a frequency-double Nd:YAG pulsed laser ($\lambda = 532\text{nm}$, repetition rate 10Hz, a duration~ 5 ns) was used. The transient decay signals were recorded by a digital oscilloscope (Tetronix TDS5052B). For the photo-CELIV measurement, the Nd-YAG pulse laser as mentioned above was applied to a solar cell device to excite photo-generated carriers and subsequently a triangular voltage ramp (DS345, Stanford Research System) was applied with reverse bias to extract photo-generated carriers after a delay time controlled by a delay generator (DG535, Stanford Research System). The extracted carriers with different controlled delay time were then recorded by a digital oscilloscope (Tetronix TDS5052B) and the corresponding carrier concentrations n were calculated by integrating conduction current over the extraction time t_{pulse} according to Ref. 25.

$$n = \frac{1}{ed} \int_0^{t_{\text{pulse}}} [j(t) - j(0)] dt \quad (1)$$

where e is elementary charge 1.6×10^{-19} C and d is thickness of the sample. $j(0)$ is the capacitive displacement current based on the Maxell's equation and mobility can be calculated in the photo-CELIV measurement by using the equation:^{23,24}

$$\mu = \frac{2d^2}{3At_{\max}^2 (1 + 0.36 \frac{\Delta j}{j(0)})} \quad (2)$$

where A is ramp speed of extraction voltage and $t_{\max}$ is the time to reach current maximum. $\Delta j = j_{\max} - j(0)$ is the extracted conduction current that contains contribution both from intrinsic and photo-generated carriers created by pulse laser. To make the time-of-flight (TOF) mobility measurement, thicker films ($\sim 2 \mu\text{m}$) were prepared by drop-casting the P3HT/TiO₂ hybrid or pristine P3HT solution onto the substrates. In the electron mobility measurement, a device with a structure of ITO/P3HT:TiO₂ hybrid layer/Al was used while in the hole mobility measurement, a semi-transparent Al electrode (35 nm) was thermally evaporated to replace the ITO electrode forming an Al/ P3HT:TiO₂ hybrid layer/Al device structure. The transparent or semi-transparent electrodes were exposed to a frequency-double Nd:YAG pulsed laser ($\lambda = 532\text{nm}$, repetition rate 10Hz, a duration ~ 5 ns) to generate thin layer of charge carriers. Under the externally applied electric field by using a Keithley 2410 source meter, these carriers were drifted toward the counter electrode, giving the transient photocurrent signal that was recorded by a digital oscilloscope (Tektronix TDS5052B). The drift mobility μ at an applied electric field E , is deduced according to $\mu = d/Et_{tr}$, where d is the thickness of the film, t_{tr} is the transit time for the arrival of carriers at the collecting electrode. The carriers (electrons or holes) under study were selected by changing the polarity of the applied electric field.