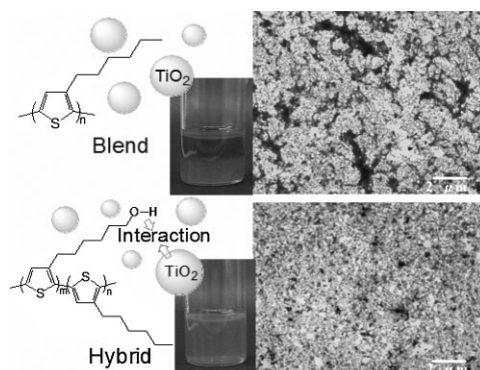


Photoactive Polythiophene:Titania Hybrids with Excellent Miscibility for Use in Polymer Photovoltaic Cells

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A series of poly{(3-hexylthiophene)-*co*-[3-(6-hydroxyhexyl)thiophene]}:titania (P3HT-OH:TiO₂) hybrids were synthesized via the in situ polycondensation of titanium (IV) *n*-butoxide in the presence of P3HT-OH. Introducing a hydroxyl moiety onto the side-chain of poly(3-hexylthiophene) (P3HT) significantly promotes the polymer-titania interaction, resulting in the formation of homogeneous hybrid colloids. The UV-vis spectra of P3HT-OH:TiO₂ films demonstrate that TiO₂ markedly affects the stacking structure and the chain conformation of P3HT-OH. The maximum absorption wavelength of these hybrid materials can be tailor-made by merely varying the weight percentage of TiO₂. Moreover, P3HT-OH:TiO₂ can be further utilized as an efficient compatibilizer in preparing photoactive P3HT:P3HT-OH:TiO₂ films with excellent miscibility. The photovoltaic cell based on such a hybrid exhibited a 2.4-fold higher value of power-conversion efficiency compared to the cell based on P3HT:TiO₂.



Introduction

Titania (TiO₂) has been widely used as an electron acceptor in fabricating polymer photovoltaic cells^[1,2] because it is a safe, environmentally stable and cheap material. Moreover, titania can be made into various shapes^[3–5] such as spheres, tubes and rods to optimize its charge transport and aggregation behavior upon blending with poly-

mers.^[1,2] However, the inherent incompatibility between the hydrophilic surface of the metal oxide and the hydrophobic conjugated polymers frequently causes macroscopic phase separation, substantially reducing the electron donor/acceptor interfacial area and carrier-dissociation efficiency. Accordingly, improving the miscibility between the polymer and the metal oxide nanoparticles is important in developing photovoltaic cells with a high efficiency. Recently, Fréchet et al.^[6] demonstrated that incorporating a thin layer of ester-functionalized polythiophene, in which the ester moieties were converted into carboxylic acid groups by heat treatment, on top of TiO₂ triples the photocurrent of the layered device of fluorine-doped tin oxide (FTO)/TiO₂/poly(3-hexylthiophene) (P3HT)/Ag. In addition, Kim et al.^[7,8] found that replacing the P3HT with a COOH-bearing poly(3-alkylthiophene) as a hole-conducting material in the FTO/TiO₂/dye/polymer/Pt device results in an

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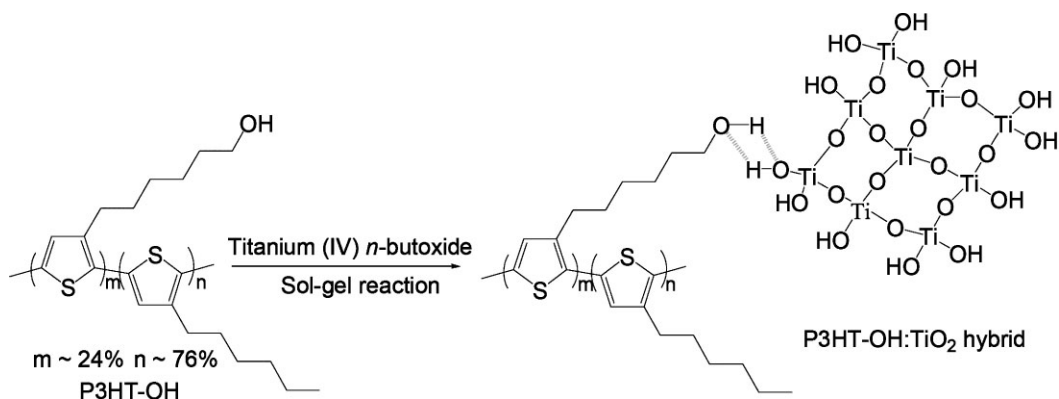
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■ Figure 1. Synthetic route to P3HT-OH:TiO₂ hybrids.

effective adsorption of the polymer on the TiO₂ surface and an enhanced cell power-conversion efficiency. However, the report on the bulk-heterojunction (BHJ) solar cells based on a stable dispersion of photoactive polythiophene:TiO₂ hybrid^[9] is still rare. In this communication, we present a new hybrid with excellent miscibility, based on a *p*-type polythiophene derivative and *n*-type TiO₂. Figure 1 illustrates the synthetic route to polythiophene:TiO₂ hybrids. Initially, the OH-containing polymer, poly{(3-hexylthiophene)-*co*-[3-(6-hydroxyhexyl)thiophene]} (P3HT-OH),^[10–15] was synthesized by copolymerizing 2-bromo-3-hexylthiophene and 2-bromo-3-(6-(2-tetrahydropyranyloxy)hexyl)thiophene^[10,11,14,15] using the McCullough approach,^[16] and treating the product with HCl. Then, the TiO₂ was prepared by the polycondensation of titanium (IV) *n*-butoxide in a solution of P3HT-OH to yield P3HT-OH:TiO₂ hybrids with various TiO₂ contents. The thus-synthesized hybrids have an excellent organic/inorganic miscibility and colloidal stability. Therefore, they can be used as a compatibilizer of P3HT and TiO₂ in fabricating polymer solar cells.

Experimental Part

Preparation of Polymer:Titania Hybrids

For chemical synthesis, all of the chemicals were purchased from the Aldrich Chemical Co. Tetrahydrofuran (THF) was dried over Na/benzophenone and freshly distilled prior to use. Other chemicals were used without further purification.

P3HT-OH was prepared in our laboratory using a method reported elsewhere.^[10,11,14–16] The molar content of the hydroxyl moiety in the polymer was determined from the ratio of the area under the resonance peak at 3.64 ppm in the ¹H NMR spectrum (using CDCl₃ as the solvent), corresponding to the methylene proton of –CH₂OH, to that under the peak at 0.87 ppm, corresponding to the methyl proton of the hexyl chain. It was found to be around 24%. The number-average molecular weight was measured by gel-permeation chromatography (GPC) analysis

(with THF as the eluent and polystyrene standards) and was found to be 17 000 g · mol⁻¹ with a polydispersity index of 1.29. Then, titanium (IV) *n*-butoxide (5.5 μL of an 11 wt.-% TiO₂ sample; 11.0 μL of a 20 wt.-% TiO₂ sample; or 22.0 μL of a 34 wt.-% TiO₂ sample) was added to a mixture of 10 mg of the P3HT-OH and 10 mL of THF. A small amount of 1 M HCl was added. The resulting mixture was stirred at a moderate speed at room temperature for 18 h to yield the P3HT-OH:TiO₂ hybrid solutions. Moreover, for comparison, a series of P3HT:TiO₂ hybrids was also synthesized following the procedure described above. The P3HT used here was polymerized by the McCullough method, described elsewhere.^[16] The molecular weight characteristics of the product determined by GPC are as follows: $\bar{M}_n = 21\,000$ g · mol⁻¹, PDI = 1.27.

Fabrication of Photovoltaic Cells

Photovoltaic devices based on polymer:TiO₂ BHJ were fabricated by spin-coating a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (≈40 nm, Baytron P VP Al 4083) on a precleaned indium tin oxide (ITO) glass substrate, and drying at 140 °C for 20 min. The polymer (10 mg · mL⁻¹) and titanium (IV) *n*-butoxide (22 μL · mL⁻¹) were dissolved in chlorobenzene, and the blend was stirred at room temperature for 36 h (humidity ≈ 70%). Then, the photoactive solution was spin-coated on top of the PEDOT:PSS layer, forming a photoactive layer of 90 nm thickness, followed by drying under vacuum (10⁻² Torr) to remove the residual solvent and TiO₂ precursor. Subsequently, an Al (150 nm) electrode was deposited on top of the photoactive layer by thermal evaporation at a pressure of around 10⁻⁶ Torr. After Al deposition, the devices were annealed at 155 °C for 3 h. The active area of the photovoltaic devices, defined by shadow mask, was 0.06 cm².

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker DMX-300 FT-NMR spectrometer. Gel-permeation chromatography (GPC) was conducted on a JASCO system that was equipped with a PU-1580 elute pump, a UV-1570 detector and two linear Jordi columns, using THF as the eluent and polystyrene

standards. UV-vis spectra were obtained using a JASCO V-570 UV/VIS/NIR spectrophotometer. Transmission electron microscopy (TEM) images were captured using a Hitachi H-7100 microscope. The samples were prepared by spin-casting the THF solution of the corresponding hybrid on a crystalline KBr substrate, before placing them in a water bath to dissolve the KBr, depositing the hybrid films that floated on the surface of the water onto a TEM copper grid and then drying them at room temperature. The current density–voltage (J – V) characteristics of the photovoltaic devices were measured with a Keithley 2400 source meter. The external quantum efficiency (EQE) spectra were recorded under illumination by a xenon lamp and a monochromator (TRIAx 180, JOBIN YVON), and the light intensity was calibrated using an OPHIR 2A-SH thermopile detector. The AM 1.5G solar irradiation was obtained from a 300 W Oriel solar simulator, and the $100 \text{ mW} \cdot \text{cm}^{-2}$ light intensity was calibrated by a mono-Si reference cell with a KG5 filter.

Results and Discussion

Figure 2a shows photographs of the solutions of P3HT-OH and the as-prepared P3HT-OH:TiO₂ hybrids in THF. Although the TiO₂ content increased from 0 to 34 wt.-%, all of the samples remained translucent and no visible aggregates formed; the color of the solutions gradually changed from red to bright orange. For comparison, the blends of P3HT and TiO₂ with various titania contents were also prepared following the same procedure as was used to synthesize P3HT-OH:TiO₂ hybrids, except that P3HT replaced P3HT-OH. Figure 2b reveals that the THF solution of P3HT is transparent, but a visible white material precipitated after the in situ sol-gel reaction of the TiO₂ precursor in all of the P3HT:TiO₂ blends. These results imply that the hydroxyl moieties in the polymer side-chains may form hydrogen bonds with Ti–OH groups on the TiO₂ surface, effectively dispersing TiO₂ and changing the conformation of the polythiophene chains. Figure 2c shows the UV-vis absorption spectra of the P3HT-OH and P3HT-OH:TiO₂ hybrid solutions. The absorption band at 440 nm corresponds to the conjugated polythiophene structure. The extent of conjugation directly influences the energy of the π – π^* transition, which appears as the maximum absorption wavelength (λ_{max}) in the absorption spectra.^[16,17] The λ_{max} of the P3HT-OH:TiO₂ solution was blue-shifted from 447 nm to 415 nm as the TiO₂ content in the hybrids increased from 0 to 34 wt.-%, consistent with the change of the color of the solution, clearly indicating that the chain conformation of P3HT-OH changed from rod-like for the pure polymer solution to a more coil-like form for the hybrid solution,^[18] because of the anchoring of TiO₂ on the polymer chain. The absorption peak at ≈ 260 nm, corresponding to TiO₂, became more pronounced as the TiO₂ content increased, revealing that the TiO₂ formed in situ was well incorporated into the polymer matrix

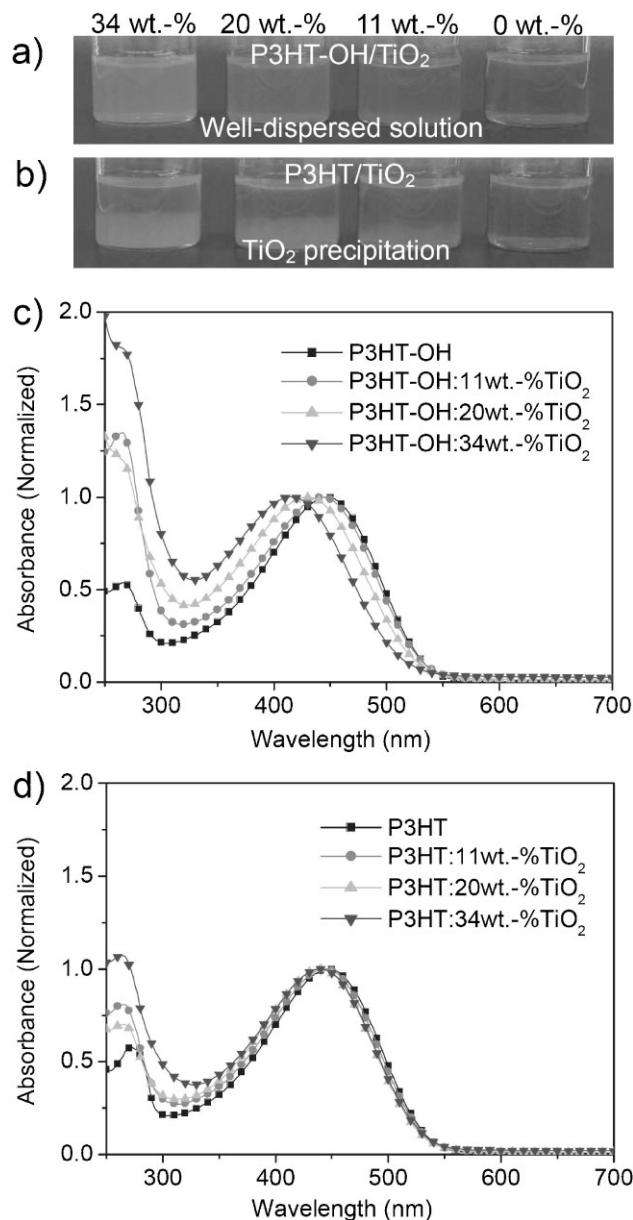


Figure 2. Photographs of the solutions of a) P3HT-OH:TiO₂ and b) P3HT:TiO₂; UV-vis absorption spectra of the solutions of c) P3HT-OH:TiO₂ and d) P3HT:TiO₂ with different TiO₂ contents.

forming a stable dispersion. Conversely, the peak intensity at 260 nm for the P3HT:TiO₂ system increased only slightly as the concentration of titanium (IV) *n*-butoxide increased during the sol-gel reaction (Figure 2d), suggesting that most of the as-formed TiO₂ precipitated out of the solution and the concentration of TiO₂ slightly increased. The λ_{max} of the P3HT was also at 447 nm but all of the P3HT:TiO₂ solutions exhibited almost no shift in λ_{max} . These results verify that the hydroxyl groups in the P3HT-OH caused a

strong polymer-particle interaction, greatly improving the stability of the TiO₂ colloids.

Figure 3(a–b) shows TEM images of films of P3HT-OH and P3HT, respectively, which contained 34 wt.-% of TiO₂ and were prepared by spin-casting the solution of the corresponding hybrids on a crystalline KBr substrate, before placing them in a water bath to dissolve the KBr, depositing the hybrid films that floated on the surface of water onto a TEM copper grid and then drying them at room temperature. The image of the P3HT-OH:TiO₂ film shows a homogeneous morphology with non-evident microscale phase separation, indicating excellent misci-

bility between the P3HT-OH and the TiO₂. In contrast, microsized TiO₂ clusters (dark region) were observed everywhere within the P3HT:TiO₂ film, proving that the poor compatibility between the hydrophobic polymer chains and the hydrophilic particle surfaces causes serious phase separation in the hybrid and uneven distribution of titania inside the P3HT matrix. Figure 3c shows the UV-vis spectra of the thin films of P3HT-OH and P3HT-OH:TiO₂ that were prepared by spin-coating the corresponding solutions on a glass slide followed by drying at room temperature. The spectrum of the P3HT-OH film is very similar to that of the P3HT film and exhibits two peaks at 554 nm and 610 nm and a shoulder at 510 nm. These three vibronic absorption bands correspond to the π - π^* transition of an ordered π -stacking structure of polythiophene.^[18] However, the peak at 610 nm of the P3HT-OH film that contained 11 wt.-% of TiO₂ was barely detectable compared to that of the pure P3HT-OH film. As the titania content was further increased to 20 and 34%, the three absorption bands merged into a blue-shifted single peak, suggesting that the highly ordered structure of the P3HT-OH chains was transformed into the disordered state, because a strong polymer-particle interaction occurred as TiO₂ particles were incorporated into the polymer matrix. Conversely, the spectra of the P3HT:TiO₂ films, shown in Figure 3d, show that the TiO₂ particles in the hybrid has very little effect on the stacking pattern of P3HT. The overall shift for P3HT-OH is more than 100 nm, revealing that increasing the TiO₂ content triggered a rod-to-coil transition. These results demonstrate that the presence of TiO₂ changes not only the stacking structure but also the chain conformation of the P3HT-OH in a solid film. Moreover, the λ_{max} (450 nm) of the P3HT-OH:TiO₂ (34 wt.-%) film is very close to that (447 nm) of a pure P3HT-OH solution, implying that all of the polymer chains were somewhat isolated by the TiO₂ domain.

Figure 4a shows plots of the external quantum efficiency (EQE) of photovoltaic cells with the structure ITO/PEDOT:PSS/active layer/Al. Here, the composites of P3HT-OH:TiO₂ or P3HT:TiO₂ were prepared at a constant polymer-to-TiO₂ weight ratio of 1:0.34 and adopted as the active layer in the BHJ device. The EQE spectra of both the P3HT-OH:TiO₂ and the P3HT:TiO₂ devices closely follow the absorption spectra of the corresponding photoactive films, revealing that light that is absorbed by the polymer contributes to the photocurrent. A comparison with the P3HT:TiO₂ device shows that the λ_{max} of the EQE of the P3HT-OH:TiO₂ device was blue-shifted, as revealed by their UV-vis absorption spectra. However, the P3HT-OH:TiO₂ device had a lower EQE at all wavelengths than the P3HT:TiO₂ device, implying poor carrier mobility on P3HT-OH, associated with the formation of the coil-like conformation of the polymer chains upon their interaction with the TiO₂ particles.

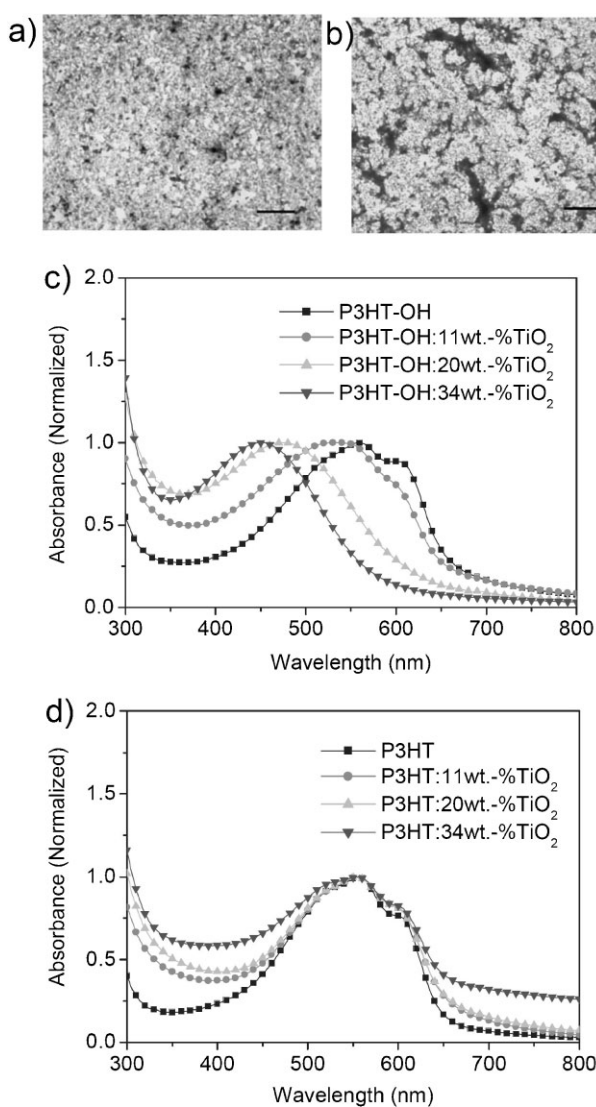


Figure 3. TEM images of the thin films of a) P3HT-OH:TiO₂ and b) P3HT:TiO₂, both with 34 wt.-% TiO₂ (scale bar = 2 μ m); UV-vis absorption spectra of c) P3HT-OH:TiO₂ and d) P3HT:TiO₂ films with different TiO₂ contents.

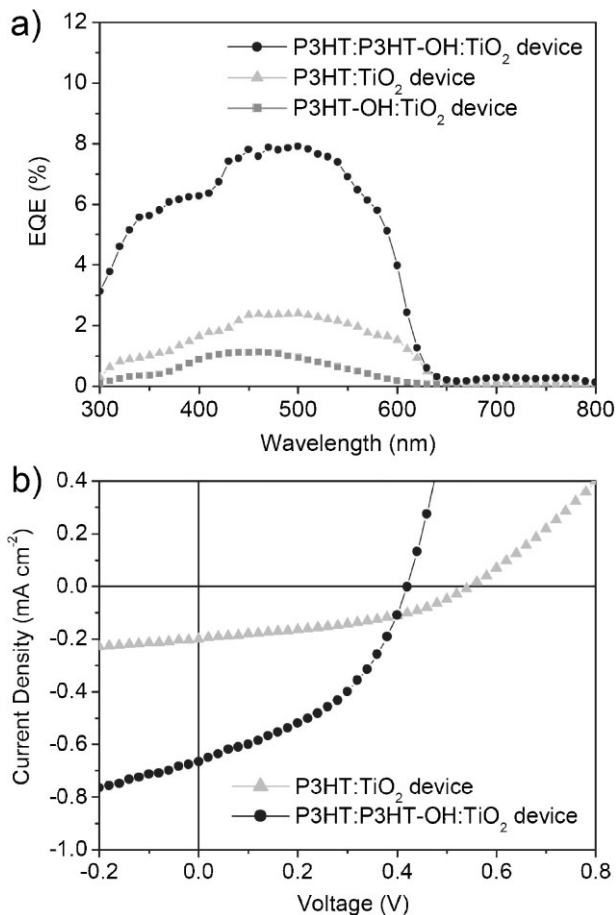


Figure 4. a) External quantum efficiency (EQE) spectra and b) current density (J)-voltage (V) characteristics ($100 \text{ mW} \cdot \text{cm}^{-2}$, AM 1.5G) of ITO/PEDOT:PSS/polymer:TiO₂/Al photovoltaic cells.

Nevertheless, incorporating a little amphiphilic diblock copolymer containing P3HT and fullerene macromonomer as a compatibilizer into the solution from which the P3HT and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) BHJ films are cast modifies the phase separation and morphology.^[19] This approach has been demonstrated to be an effective method of improving device performance. Accordingly, P3HT-OH:TiO₂ was also employed as a compatibilizer for preparing P3HT:P3HT-OH:TiO₂ hybrids. Herein, the TiO₂ particles were synthesized *in situ* by the sol-gel route, as described above, in a solution of P3HT that also contained 10 wt.-% of P3HT-OH. The thus-synthesized hybrids had good colloidal stability and no obvious precipitation was observed after storage under ambient conditions for several days. For comparison, the P3HT:TiO₂ blend was prepared similarly, but without the addition of P3HT-OH. Figure 4b plots the J - V curves of the devices of ITO/PEDOT:PSS/P3HT:P3HT-OH:TiO₂ (or P3HT:TiO₂)/Al

under AM 1.5G solar irradiation at an intensity of $100 \text{ mW} \cdot \text{cm}^{-2}$. The P3HT:TiO₂ device exhibited poor cell performance with an open-circuit voltage (V_{OC}) of 0.55 V, a short-circuit current density (J_{SC}) of $0.20 \text{ mA} \cdot \text{cm}^{-2}$, a fill factor (FF) of 41.2%, and a power-conversion efficiency (PCE) of 0.05%. In contrast, the P3HT:P3HT-OH:TiO₂ device had a significantly improved J_{SC} . A PCE of 0.12% with $J_{\text{SC}} = 0.67 \text{ mA} \cdot \text{cm}^{-2}$, $V_{\text{OC}} = 0.43 \text{ V}$ and FF = 42.3% was achieved. Moreover, the EQE of the P3HT:P3HT-OH:TiO₂ device (EQE = 7.9% at 500 nm) was 3.3-fold higher than that of the P3HT:TiO₂ device (EQE = 2.4% at 500 nm) (shown in Figure 4a). These results suggest that blending P3HT-OH:TiO₂ into P3HT notably increases the polymer/titania compatibility, substantially increasing the photoinduced charge-transfer efficiency and thus improving the device performance.

Conclusion

A new approach for synthesizing stable polythiophene:TiO₂ hybrid dispersions with the aid of OH-bearing polythiophene was demonstrated. The hydroxyl group on the polymer side-chain effectively prevents the macroscopic aggregation of TiO₂ during the sol-gel reaction because of the strong polymer-particle interaction, producing a uniform distribution of TiO₂ throughout the polymer matrix in the hybrid solutions and hybrid films. Very interestingly, the quantity of titania particles in P3HT-OH:TiO₂ films strongly influences both the stacking pattern and the chain conformation of P3HT-OH. Thus, the absorption spectrum of the hybrid film can be fine-tuned and the absorption maximum can be shifted by more than 100 nm simply by varying the TiO₂ content, enabling these novel hybrids to be further applied as photosensitive materials in polymer photosensors. Replacing titania with a high-band-gap material such as silica potentially enables the development of such a hybrid as a photoluminescent material with tunable emission color. Moreover, P3HT-OH:TiO₂ was found to be an efficient compatibilizer in preparing miscible P3HT:P3HT-OH:TiO₂ films. The photovoltaic cell based on such a hybrid has J_{SC} and PCE values that are around 3.4-fold and 2.4-fold higher, respectively, than those of the device based on the P3HT:TiO₂ blend without added P3HT-OH:TiO₂.

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