Band gap aligned conducting interface modifier enhances the performance of thermal stable polymer-TiO$_2$ nanorod solar cell

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In this paper, we show that the poly(3-hexyl-thiophene)/TiO$_2$ nanorod hybrid material is more thermally stable than the poly(3-hexyl-thiophene)/[6,6]-phenyl C$_{61}$-bntyric acid methyl ester (P3HT/PCBM) hybrid material. A metal free conducting interface modifier of oligo-3-hexyl thiophene carboxylic acid (oligo-3HT-COOH) has been synthesized that exhibits aligned band gap for the P3HT/TiO$_2$ hybrid. The conducting modifier shows an increase in power conversion efficiency of 4.8 times over an insulating modifier of oleic acid and 2.2 folds improvement over small molecule modifier of pyridine. These increases are due to a reduced recombination rate (42 μs carrier life time) and fast electron injection time of 0.24 ps. This interface modifier makes thermally stable organic-inorganic hybrid materials useful for fabrication of all solution processable solar cells. © *2010 American Institute of Physics*. [doi:10.1063/1.3357425]

Nanocomposites made from conducting polymer-nanoparticle hybrid are attractive for use in solar cells because of their light weight, low cost, high throughput, and nonvacuum processing by using reel-to-reel or spray deposition on flexible substrates. These materials also offer the potential for very thin and flexible photovoltaic devices with high energy densities.[1,2] The working principle of hybrid solar cell[3–5] is such that the conducting polymers can harvest sun light and using transport holes, the nanoparticles can transport electrons while maintaining charge separation. At present, there are two kinds of hybrid materials being developed for solar cells. One is a polymer-fullerene derivative and the other is polymer-semiconducting nanoparticle. The intimate miscibility between polymer and fullerene derivatives has resulted in higher power conversion efficiency[6–8] versus those hybrid materials made from polymer-semiconducting nanoparticles.[9] However, the fullerene of the polymer-fullerene hybrids start to aggregate at 140 °C and form a large aggregate (>1 μm) at 150 °C that interrupts the required bicontinuous morphology of the hybrid film necessary for solar cell applications.[10] On the other hand, semiconducting nanoparticle hybrids are expected to have better thermal stability than the polymer-fullerene hybrid due to the inherent temperature resistant character of compounds such as TiO$_2$. Therefore, good thermal stability hybrids are desired for the fabrication of long life solar cells.

While semiconducting nanoparticles exhibit hydrophilic character, polymers are hydrophobic; so, there is a need to use an interface modifier to render the nanoparticles compatible with both the polymer and organic solvent. The interface modifier must also have dual functions as a barrier and a conductor. The barrier function is to (1) reduce the recombination of charge carriers and (2) reduce trapping charge carriers at the surface defects of nanoparticles. The conducting

function with an aligned band gap will then facilitate both charge injection and charge transport in the solar cell. We have used organic molecules with end functional carboxylic acid moieties and ruthenium dye to modify the surface of TiO$_2$ nanoparticles. Our selection is based on their compatibility with poly(3-hexylthiophe) (P3HT) and TiO$_2$. Moreover, they can effectively reduce electron-hole recombination.[9]

For TiO$_2$, our low cost, noble metal free conducting oligomer with a carboxylic acid end functional group is expected to be a better interface modifier than other organic molecules. Its large size can be an effective barrier and its conducting behavior allows efficient transport and injection of charge carriers. In this study, we show that the P3HT/TiO$_2$ hybrid is more thermally stable than the P3HT/PCBM hybrid. We have also demonstrated the oligo-3-hexyl thiophene carboxylic acid (oligo-3HT-COOH) is a very effective interface surface modifier for enhancing the performance of P3HT/TiO$_2$ nanorod solar cells.

We monitored the thermal stability of our nanocomposite thin film by using thermal gravimetric analysis (TGA, TA Instrument, 2950) and thermal atomic force microscopy (thermal AFM, Digital Instrument, Nanoscope III). A 1% solution of the hybrid material was prepared by blending the P3HT with nanoparticles at a weight ratio of 1:0.8 in chlorobenzene for the P3HT/PCBM system.[10] For P3HT/TiO$_2$ system, the P3HT was dissolved in chlorobenzene, then mixed with pyridine modified TiO$_2$ nanorods in a cosolvent consisting of pyridine, dichloromethane, and chloroform in a volumetric ratio of 1:2:2. The P3HT was synthesized according to the literature[11] with a molecular weight (mol. wt.) of 61881 g mol^{-1}, a polydispersity index (PDI) of 1.48 and a regioregularity (RR) of 97.2%. The pyridine modified TiO$_2$ was also synthesized according to the literature.[9] Films for TGA were obtained from hybrid solution by drop casting and drying in a vacuum oven at 100 °C overnight. TGA was then
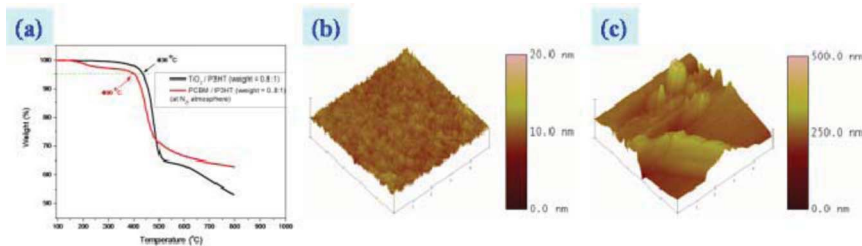
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FIG. 1. (Color online) Thermal stability study of polymer-nanoparticle hybrid materials by (a) thermal gravimetric analysis and thermal AFM [(b) and (c)]. Thermal AFM images of (b) P3HT/TiO$_2$ nanorods films and that of (c) P3HT/PCBM films at 150 °C are shown.

performed at 2 °C/min starting from room temperature to 800 °C in nitrogen. The temperature at 5% weight loss of sample was recorded as the thermal decomposition temperature. The film for thermal AFM was obtained by spin coating at 1000 rpm for 60 s on indium-tin-oxide (ITO) glass.[10] During thermal AFM measurements (Digital Instruments, Nanoscope III) we used an extra controller to apply heat to the sample and control the temperature of the sample. The temperature was increased at 5 °C/min and held for 2 min to stabilize the temperature before AFM image capture. Figure 1(a) shows that the thermal decomposition temperature of P3HT/TiO$_2$ hybrid is 36 °C higher than that of P3HT/PCBM. Figure 1(b) clearly indicates the morphology of P3HT-TiO$_2$ hybrid did not change upon heating to 150 °C. However, large aggregates P3HT/PCBM hybrid formed at 150 °C [Fig. 1(c)]. These results indicate that P3HT/TiO$_2$ is more thermally stable than P3HT/PCBM, possibly because TiO$_2$ is denser and less mobile than PCBM. We have synthesized the oligo-3-hexyl thiophene (mol. wt.: 6027 g mol^{-1}, PDI: 1.27, RR: 76%) via Suzuki coupling method.[12,13] The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the oligomer was measured by cyclic voltammetry (CH Instruments, 40524A). Figure 2 shows the chemical structure of oligomer and its band gap as related to the P3HT and TiO$_2$. The oligomer is well aligned between the polymer and nanorods which enabling efficient charge transport.

The oligo-3HT-COOH modified TiO$_2$ nanorod was prepared by refluxing the mixture of pyridine modified nanorods and oligomer (wt. ratio 1:0.023) at 70 °C for 24 h in pyridine and N$_2$. Then, the solution was cooled to room temperature. Excess hexane was used to precipitate TiO$_2$ and to wash out any nonadsorbed oligomer. Finally, the oligo-3HT-COOH modified TiO$_2$ nanorods were collected after subsequent centrifugation and drying processes. By using the laser flash photolysis system (Edinburgh, LP920) and the femtosecond transient absorption system (Spectra-Physics, Spitfire Pro system); we measured the recombination times of TiO$_2$-pyridine and TiO$_2$-(oligo-3HT-COOH) to be 42 μs and 12 ms, respectively (Fig. 3). The half life of electron injection of TiO$_2$-(oligo-3HT-COOH) was measured to be 0.24 ps which, is a little less than the Ru based dye N3 of 0.4 ps.[14] These results indicate that the oligomer can significantly reduce charge recombination and facilitate the charge transport.

For the solar cell study, the hybrid material was prepared by blending the oligo-3HT-COOH modified TiO$_2$ with P3HT in 53:47 wt/wt ratio. A ~120 nm thick hybrid material was spin coated on ITO glass covered with about 40 nm poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Baytron P, 4083). The PEDOT-PSS layer was then spin coated onto ITO and baked at 120 °C for 30 min. The conducting behavior of the hybrid at nanoscale was studied by conducting AFM (Veeco, CP-II). Figure 4 shows that the conductivity is higher and the charge distribution is smoother for hybrids made from the oligo-3HT-COOH modified TiO$_2$ as compared with samples prepared using oleic acid modified TiO$_2$ or pyridine modified TiO$_2$. This means that the P3HT/TiO$_2$-(oligo-3HT-COOH) hybrid has the most efficient charge transport among different interface modifiers.

The solar cells were fabricated by spin coating the hybrid to thickness of ~120 nm on the ITO glass covered with about 40 nm PEDOT:PSS as described before. Then, a layer of pristine TiO$_2$ nanorods (about 20 nm) was subsequently spin coated on top of the active layer as a hole blocking layer.[5] Finally, an Al (100 nm) cathode was deposited on the top of device by thermal deposition. The performance of these devices were evaluated under AM 1.5G irradiation (100 mW cm^{-2}) using a solar simulator (Oriel Inc.). The efficiency can be increased by 4.8 times using this oligomer modified TiO$_2$ as compared with oleic acid modified TiO$_2$. The results are summarized in Table I.

We measured the carrier mobility using the space charge limiting current technique. The hole mobility is 1.2 × 10^{-3} cm^2/V s and the electron mobility is 1.5 × 10^{-5} cm^2/V s. The relative low power conversion efficiency of P3HT/TiO$_2$ hybrid system as compared with the P3HT/PCBM hybrid system is due to this three order difference in unbalanced charge mobility. The result of balancing the carrier mobility to improve the cell's efficiency is among our ongoing research. We plan to report the results sometime in the near future.
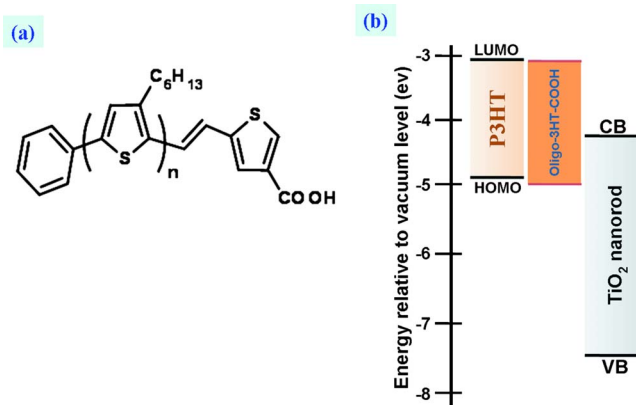

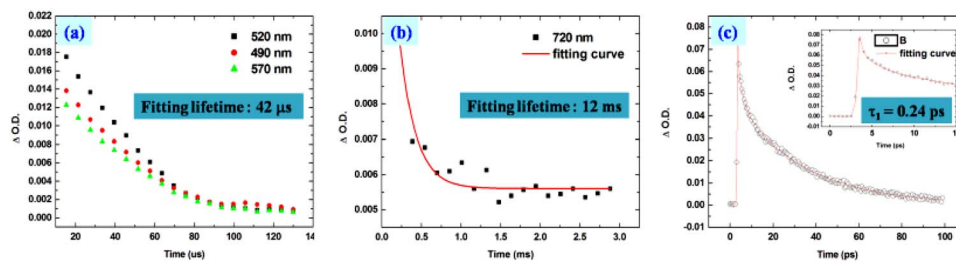FIG. 2. (Color online) (a) Chemical structure of oligo-3HT-COOH and (b) band diagram of P3HT-(oligo-3HT-COOH)-TiO$_2$.

FIG. 3. (Color online) Recombination rate of (a) pyridine and (b) oligo-3HT-COOH modified TiO_2 and (c) half life of electron injection of oligo-3HT-COOH modified TiO_2 measured by transient absorption spectroscopy.
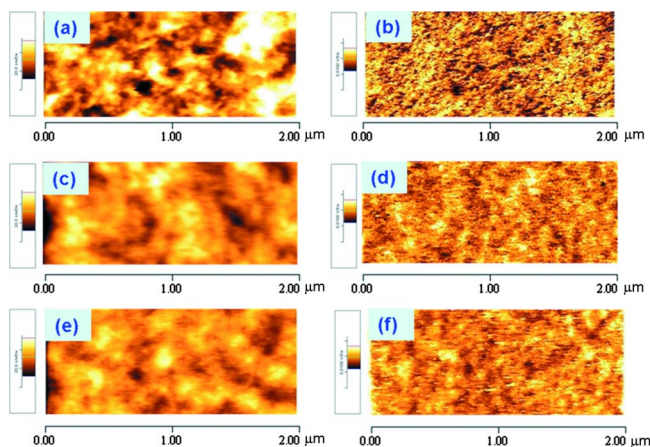

FIG. 4. (Color online) Surface morphology (left column) and conductivity distribution images (right column) of P3HT/TiO_2 nanorod hybrids using modifier of [(a) and (b)] oleic acid, [(c) and (d)] pyridine, and [(e) and (f)] oligo-3HT-COOH.

TABLE I. Performance of P3HT/TiO_2 nanorod solar cell using different interface modifier under A.M. 1.5 illumination (100 mW/cm^2).

Interface modifier	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
P3HT/TiO_2-(oleic acid)	0.65	1.17	0.35	0.27
P3HT/TiO_2-(pyridine)	0.61	1.71	0.56	0.59
P3HT/TiO_2-(oligo-3HT-COOH)	0.64	3.26	0.62	1.29

In summary, we have found the P3HT/TiO_2 nanorod hybrid material is more thermally stable than a P3HT/PCBM hybrid material in solar cell applications. A noble metal free conducting interface modifier of oligo-3-hexyl thiophene carboxylic acid was shown to enhance power conversion efficiency for P3HT/TiO_2 nanorod hybrid solar cells. The results are due to the faster transport and injection of charge carriers of this oligomer as compared with an insulating modifier of oleic acid or a small molecular modifier of pyridine. We demonstrate the surface modifier retards recombination and improves electron injection rate in a highly efficient way. The oligomer is also shown its ease to anchor onto TiO_2 surface and has great potential in solar cells application in the future.

[1]C. A. Mayer, S. R. Scully, B. E. Hardin, M. W. Rowell, and M. D. McGehee, Mater. Today **10**, 28 (2007).
[2]C. J. Brabec and J. R. Durrant, MRS Bull. **33**, 671 (2008).
[3]N. C. Greenham, X. Peng, and A. P. Alivisatos, Phys. Rev. B **54**, 17628 (1996).
[4]M. C. Scharber, D. Muhlbacher, M. Koppe, P. Denk, C. Waldant, A. J. Heeger, and C. J. Barbec, Adv. Mater. **18**, 789 (2006).
[5]T. W. Zeng, Y. Y. Lin, H. H. Lo, C. W. Chen, C. H. Chen, S. C. Liou, H. Y. Huang, and W. F. Su, Nanotechnology **17**, 5387 (2006).
[6]C. W. Liang, W. F. Su, and L. Y. Wang, Appl. Phys. Lett. **95**, 133303 (2009).
[7]S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, and A. J. Heeger, Nat. Photonics **3**, 297 (2009).
[8]J. Hou, H. Y. Chen, S. Zhang, R. I. Chen, Y. Yang, Y. Wu, and G. Li, J. Am. Chem. Soc. **131**, 15586 (2009).
[9]Y. Y. Lin, T. H. Chu, S. S. Li, C. H. Chuang, C. H. Chang, W. F. Su, C. P. Chang, M. W. Chu, and C. W. Chen, J. Am. Chem. Soc. **131**, 3644 (2009).
[10]Y. C. Huang, S. Y. Chuang, M. C. Wu, H. L. Chen, C. W. Chen, and W. F. Su, J. Appl. Phys. **106**, 034506 (2009).
[11]M. C. Iovu, E. E. Sheina, R. R. Gil, and R. D. McCullough, Macromolecules **38**, 8649 (2005).
[12]J. Liu, T. Tanaka, K. Sivula, A. P. Alivisatos, and J. M. J. Frechet, J. Am. Chem. Soc. **126**, 6550 (2004).
[13]R. H. Lohwasser, J. Bandara, and M. Thelakkat, J. Mater. Chem. **19**, 4126 (2009).
[14]Y. Tachibana, M. K. Nazeeruddin, M. Gratzel, D. R. Klug, and J. R. Durrant, Chem. Phys. **285**, 127 (2002).