

Improved Hybrid Organic-Inorganic Photovoltaics via *In Situ* UV-Polymerization in Nanotube Arrays

Sanja Tepavcevic¹, Seth B. Darling², Nada M. Dimitrijevic², Tijana Rajh², and Steven J. Sibener¹

¹ James Franck Institute and Department of Chemistry, University of Chicago

² Center for Nanoscale Materials, Argonne National Laboratory

Research Achievement

Hybrid solar cells have been developed in the past decade as a promising alternative for traditional silicon-based solar cells. One approach for making inexpensive inorganic-organic hybrid photovoltaic (PV) cells is to fill nanostructured titania films with solid organic hole conductors such as conjugated polymers.^[1] These compounds can function as light-absorbing species and inject electrons into the conduction band of the n-type semiconductor, while at the same time they conduct the holes to the cathode. Nanotube films offer a distinct advantage over nanoparticle films in that they facilitate charge carrier transport.

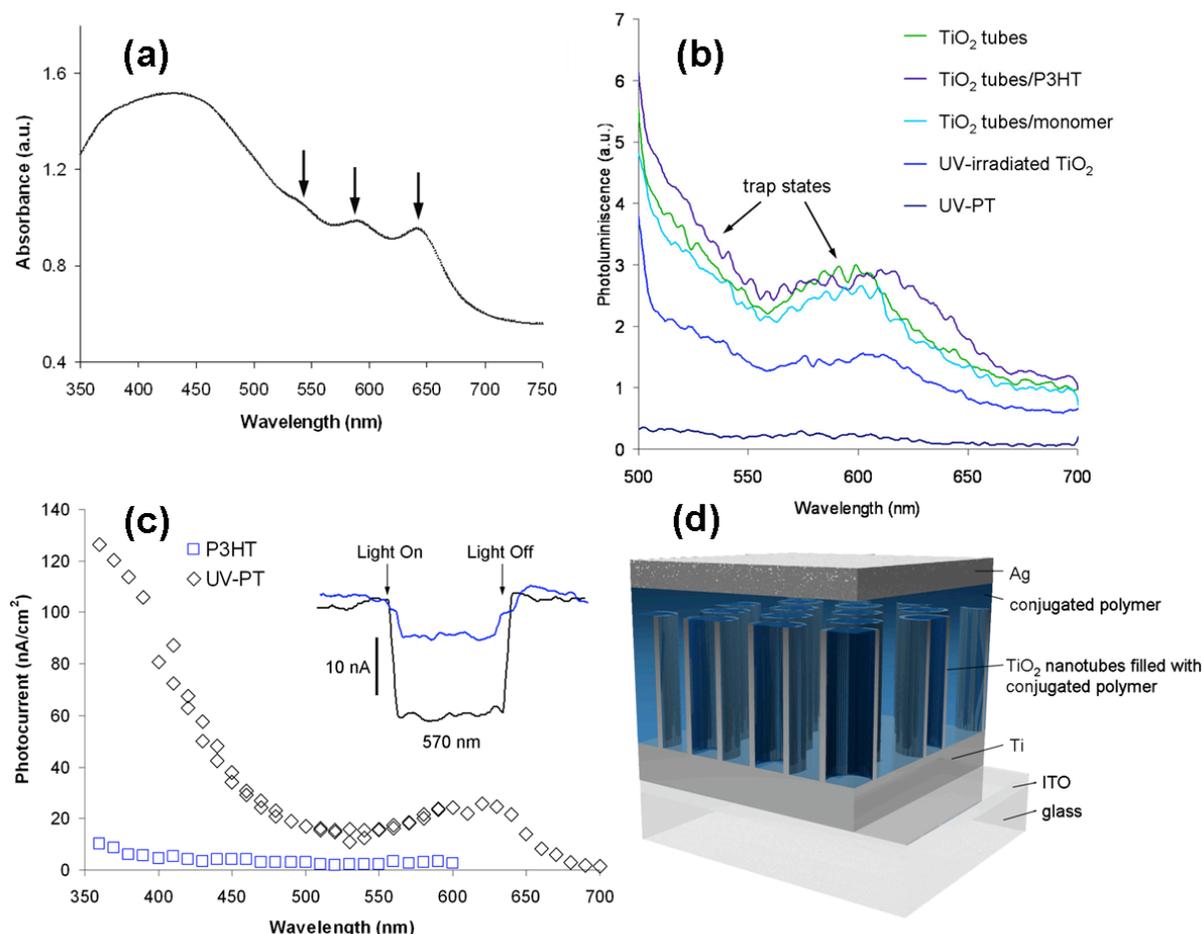
The infiltration of the polymer into the nanostructured metal oxide is of particular importance for optimizing the performance of these hybrid devices.^[2] Most of the reports on solar cells using conjugated polymers have employed wet processing deposition techniques.^[3-5] Since polymers suffer a loss of conformational entropy when they are confined in a channel whose radius is less than their radius of gyration, filling the pores with a polymer has been a challenge due to the possibility of the polymer chains clogging the pores of the nanotubular electrode.^[1]

In this project we developed a new technique for deposition/infiltration of conjugated polymer into densely ordered TiO₂ nanotube arrays. In particular, we report the effects of *in situ* ultraviolet (UV) polymerization of polythiophene vs. infiltration of pre-synthesized P3HT on the performance of solar cell devices. In our simple and efficient photochemical approach, a nanotubular TiO₂ substrate is immersed in a 2,5-diiodothiophene monomer precursor solution and then irradiated with UV light in an argon environment. The selective UV photodissociation of the C–I bond ($\lambda = 250\text{--}300\text{ nm}$) in the precursor molecule produces monomer radicals with intact π -ring structure. Since the C–I bonds are present at the ends of the reaction coupling products, further photodissociation can take place forming oligomeric and polymer species that can couple to and self-assemble on the surface of TiO₂ nanotubes (Figure [d]).^[6] The formation of polymeric semiconductor films by this method offers distinct advantages such as cost, uniformity, and scalability over other solution processing techniques. By polymerizing conjugated polymer inside an electron-accepting nanotube array, we have achieved significant improvements in optoelectronic device performance compared to those fabricated by infiltrating tubes with *ex situ*-synthesized polymer (Figure [c]). Our preparation leads to a strong coupling at the polymer-oxide interface, which is important for efficient exciton separation (Figure [b]), and fewer conformational defects (Figure [a]), which facilitates hole transport. The small molecule precursor also presumably achieves superior filling within the confined environment.

Future Work

One way to further improve performance of these hybrid cells is to maximize the light-harvesting capability through the construction of a rainbow solar cell.^[7] An example would employ TiO₂ nanotubes packed with an ordered assembly of different-length oligothiophenes. As white light enters the cell, shorter oligothiophenes (larger band gap) will absorb the portion of the incident light with smaller wavelengths. Longer wavelength light, transmitted through the initial layer, will be absorbed by subsequent layers, and so on. By using *in situ* UV

polymerization, a gradient of different length oligothiophenes can be readily created by varying UV exposure time. By constructing an ordered gradient of conjugated oligomers/polymer, it should be possible to increase the effective capture of incident light.



(a) UV-Vis absorption spectrum of polythiophene polymerized within TiO₂ nanotubes showing vibronic peaks; (b) photoluminescence spectra of TiO₂ nanotubes with various molecular fillers; (c) photoaction spectra of P3HT/TiO₂ and UV-PT/TiO₂ devices and time traces of photocurrent (inset); (d) schematic of hybrid solar cell construction

References

- [1] K. Shankar, G. K. Mor, H. E. Prakasham, O. K. Varghese, C. A. Grimes, *Langmuir* **2007**, *23*, 12445.
- [2] K. M. Coakley, Y. Liu, M. D. McGehee, K. L. Frindell, G. D. Stucky, *Adv. Func. Mater.* **2003**, *13*, 301.
- [3] K. M. Coakley, M. D. McGehee, *Appl. Phys. Lett.* **2003**, *83*, 3380.
- [4] A. C. Arango, L. R. Johnson, V. N. Bliznyuk, Z. Schlesinger, S. A. Carter, H.-H. Hörhold, *Adv. Mater.* **2000**, *12*, 1689.
- [5] P. A. van Hal, M. P. T. Christiaans, M. M. Wienk, J. M. Kroon, R. A. J. Janssen, *J. Phys. Chem. B* **1999**, *102*, 4352.
- [6] S. H. Kim, S. Natarajan, G. Liu, *Catal. Today* **2007**, *123*, 104.
- [7] A. Kongkanand, K. Tvrđy, K. Takechi, M. Kuno, P. V. Kamat, *J. Am. Chem. Soc.* **2008**, *130*, 4007.

Publication

“Improved hybrid solar cells via in situ UV-polymerization,” S. Tepavcevic, S.B. Darling, N.M. Dimitrijevic, T. Rajh, and S.J. Sibener, *Small* (2009). DOI: 10.1002/smll.200900093.