

Titanium dioxide nanotube arrays improve solar cells

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Exquisite control over an anodically formed TiO₂ nanotube array architecture, large internal surface area, and lower recombination allows for low-cost high-efficiency hybrid inorganic-organic solar cells.

The principal drive toward fabricating nano-dimensional materials lies in the promise of achieving unique properties and superior performance due to these materials' inherent nano-architectures. Titanium dioxide is a particularly versatile material with many technological applications, including a photocatalyst, photovoltaic material, gas sensor, optical coating, structural ceramic, electrical varistor, biocompatible material for bone implants, and a spacer material for magnetic spin valve systems. Therefore, the ability to control nanoscale TiO₂ architectures can be expected to positively impact many technologies.

In conjunction with a suitable organic dye or semiconductor, TiO₂ is a key material for low cost, large area, excitonic photovoltaic cells.¹ Titania nanotubes fabricated by anodization are ordered, high aspect ratio structures with nanocrystalline walls oriented perpendicular to the substrate. These nanotubes have a well-defined and controllable pore size, wall thickness, and tube-length (see Figure 1). For a 20 μ m nanotube array, the effective surface area is approximately 3000 times that of a planar unstructured surface. Like most one-dimensional structures, this high-aspect ratio nanotube array architecture promotes efficient harvesting of photons by orthogonalizing the processes of light absorption and charge separation.² The tube geometry is unique in that it allows for an active material to be either conformally coated on the walls of the nanotubes (where the large surface area is utilized), or filled into the pores of the semiconductor, which promotes efficient exciton harvesting.

We have fabricated two varieties of nanotube arrays, so-called transparent and non-transparent. Non-transparent nanotube arrays are grown on an opaque metallic Ti substrate, while transparent nanotubes are formed by anodizing a Ti film sputtered onto a conductive glass substrate. We have optimized processes to fabricate opaque nanotubes up to 1mm in length, although calculations indicate that ~30–40 μ m long nanotube arrays are

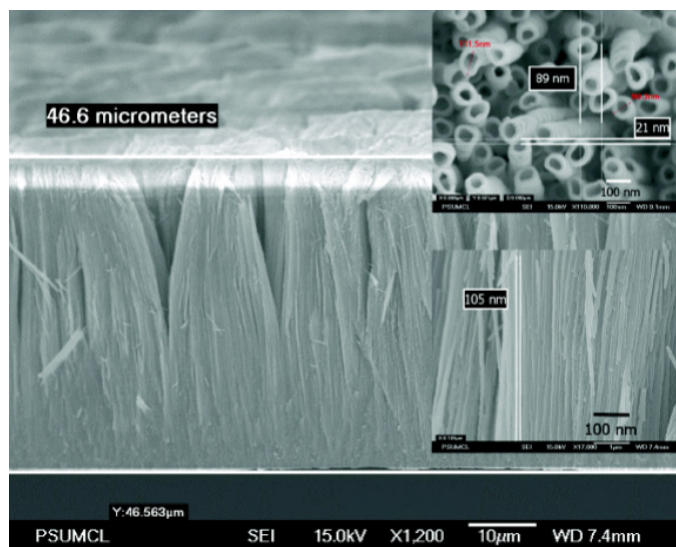


Figure 1. Field-emission scanning electron microscopy (SEM) image of a 46.6 μ m long TiO₂ nanotube array. The insets show the top view [top right] and cross-section [bottom right] of the arrays at higher magnification.

optimal to maximally harvest light without suffering losses. The optimization of our processes to produce transparent nanotubes is ongoing, and we are currently able to reproducibly make nanotubes 4 μ m long. Transparent nanotubes lend themselves to frontside illumination, which avoids photonic losses due to absorption by the platinized counter electrode and the redox electrolyte in dye-sensitized solar cells. Backside illumination geometry, where the aforementioned photonic losses occur, is the only mode of illumination possible for non-transparent nanotube arrays.

Our research group pioneered the development of transparent and non-transparent titanium dioxide nanotube arrays.^{3,4} We were the first to report functioning dye-sensitized solar cells using TiO₂ nanotube arrays in both frontside and backside illumination geometries (see Figure 2).⁵ We have demonstrated liquid

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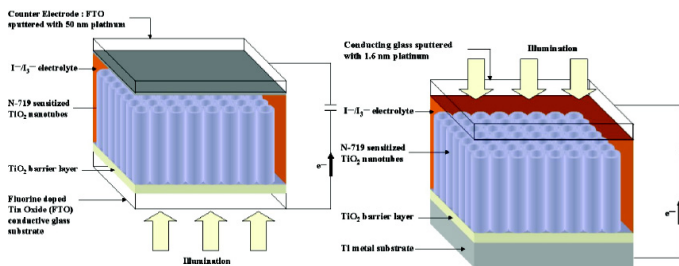


Figure 2. Schematics of illumination geometries. [left] Frontside geometry with a transparent TiO₂ nanotube array. [right] Backside geometry with a non-transparent TiO₂ nanotube array.

junction dye-sensitized solar cells with an efficiency of up to 7% using commercially available ruthenium bipyridine containing sensitizer N-719.⁶ More recently, we have been investigating other sensitizers, including donor antenna dyes and carboxylated polythiophenes.

A principal limitation of the widely used nanoparticulate TiO₂ electrodes is that electron transport occurs through trap-limited diffusion, a slow process that allows for back-electron transfer. The concomitant recombination losses limit device efficiencies, especially at longer wavelengths. Preliminary studies of electron transport and recombination in TiO₂ nanotube arrays indicate that the recombination lifetimes of photogenerated charge carriers are longer than those of nanoparticulate electrodes. However, the transport times are similar due to the nanocrystalline nature of the tube walls (typical grain size ~100nm). We are, therefore, pursuing various strategies to increase the grain size and improve the crystallinity of the nanotube arrays.

We are also actively investigating the possibility of using TiO₂ nanotubes to improve the performance of bulk heterojunction polymeric solar cells. One strategy involves confining the semi-conducting polymer blend in the nanotubes. This confinement alleviates the problem of segregation of the polymer phases, provides a second heterojunction (n-type TiO₂) for charge separation, and uses the nanotube architecture as an electron-accepting network to limit electrical dead ends in the polymeric device. As shown in Figure 3, by infiltrating our nanotubes with a blend of a hole transporting polymer, poly(3-hexylthiophene), and a methanofullerene, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), we have obtained 4.1% efficient solid-state double heterojunction solar cells.⁷

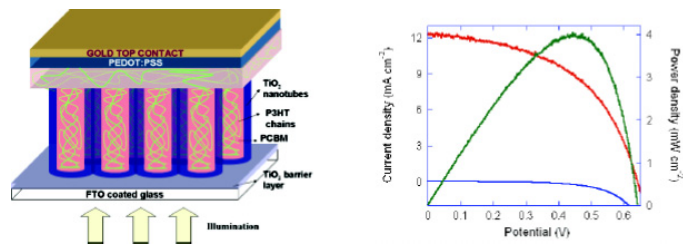


Figure 3. [left] Schematic illustration and [right] electrical characteristics of a double heterojunction solid state solar cell incorporating TiO₂ nanotubes.

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References

1. M. Gratzel, *The advent of mesoscopic injection solar cells*, **Prog. Photovoltaics** **14**, pp. 429–442, 2006.
2. N. S. Lewis, *Toward cost-effective solar energy use*, **Science** **315**, pp. 798–801, 2007.
3. G. K. Mor, O. K. Varghese, M. Paulose, and C. A. Grimes, *Transparent highly ordered TiO₂ nanotube arrays via anodization of titanium thin films*, **Adv. Funct. Mater.** **15**, pp. 1291–1296, 2005.
4. D. Gong et al., *Titanium oxide nanotube arrays prepared by anodic oxidation*, **J. Mater. Res.** **16**, pp. 3331–3334, 2001.
5. G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, *Use of highly-ordered TiO₂ nanotube arrays in dye-sensitized solar cells*, **Nano Lett.** **6**, pp. 215–218, 2006.
6. K. Shankar, G. K. Mor, H. E. Prakasam, S. Yoriya, M. Paulose, O. K. Varghese, and C. A. Grimes, *Highly-ordered TiO₂ nanotube arrays up to 220 μm in length: use in water photoelectrolysis and dye-sensitized solar cells*, **Nanotechnology** **18**, 2007.
7. G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, *High efficiency double heterojunction polymer photovoltaic cells using highly ordered TiO₂ nanotube arrays*, **Appl. Phys. Lett.** **91**, 2007.