Titania photovoltaic cell performance

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Optimization of annealing conditions significantly increases the short-circuit current density of nanotube-based solar cells.

The high demand for efficient and inexpensive renewable energy sources is leading to increased research in organic photovoltaics. Among the different types of devices, dye-sensitized solar cells (DSSCs) based on porous titanium dioxide (TiO$_2$) nanoparticle layers$^1$ can achieve the highest efficiency, exceeding 10%. However, electron transport through a random TiO$_2$ network is typically very slow.$^2$ Improving its performance means developing novel organic dyes. Alternatively, replacing the TiO$_2$ layer with one having a different nanostructure could also potentially achieve both improved charge transport and collection.

To this end, one could employ 1D nanostructures such as nanowires or nanotubes. Yet though 1D arrays enable simple pathways for electrons to reach electrodes, they also have smaller surface areas compared to random nanoparticle networks, thus leading to reduced performance. For example, the efficiency$^3$ of 6.89% for an $\sim 20\mu$m-long DSSC made of TiO$_2$ nanotube arrays is still lower than that routinely achieved using a porous layer. Because increased surface areas can be obtained using longer nanotubes of smaller diameter, much effort has been invested in developing novel anodization procedures aimed at improving nanotube form and structure.$^3$–$^6$ Anodization conditions such as those determined by the type of electrolyte or the voltage applied, among others, measurably affect the morphology of the nanotubes (see Figure 1). However, the specific fabrication procedure employed also determines the crystal quality, as well as the defect types and densities, which in turn regulate charge transport.

We have studied the effects of the synthesis methods used on the charge transport, composition, and photovoltaic performance of TiO$_2$ nanotube arrays. We found that both the electrolytes used and the annealing environment influence the efficiency of the titania-nanotube-based solar cells.$^7$

Figure 1. TiO$_2$ nanotubes obtained using electrolytes containing (a) ammonium fluoride and ethylene glycol$^3$,$^5$ and (b) potassium fluoride (KF).$^6$,$^7$ (c) Side view of the tubes resulting from KF electrolyte use.

The annealing temperature, too, has a significant effect on cell performance because it determines the crystal structure of the nanotubes. If annealing occurs at the same temperature in air and ammonia, the crystal structure does not change (anatase). On the other hand, the composition of the nanotubes (i.e., the oxygen-to-titanium ratio) depends strongly on the ambient atmosphere. Annealing in ammonia typically results in alterations in the shape of the oxygen peak and lower oxygen-to-titanium ratios, as observed in x-ray photoelectron spectroscopy.$^7$

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The observed effect on solar cell performance is an increase in the short-circuit current density and a simultaneous decrease in the fill factor. This results in an overall efficiency increase. In optimal annealing conditions, the short-circuit current density and power-conversion efficiency of 4.27 mA cm\(^{-2}\) and 1.30%, respectively, could be achieved for 2\(\mu\)m-long nanotubes, as shown in Figure 2.

The beneficial effects of annealing in ammonia with respect to air also apply to other morphologies of TiO\(_2\)/titanate nanostructures. In this context, significant improvements are measured in the short-circuit current density of titania-nanowire-based DSSCs. Just as for nanotubes, a small decrease in the fill factor is observed, whereas the overall performance is significantly improved: an efficiency of 1.88% is achieved for optimal conditions.

While these results are still lower than those of DSSCs made of porous titania films, we have demonstrated the promise of optimizing annealing conditions for TiO\(_2\). The best atmosphere is similar for different morphologies, so that further improvements in DSSC performance can likely be secured using nanostructured networks of large surface area and conducive to efficient electron transport, such as mixtures of nanowires or nanotubes and nanoparticles.

Figure 2. Current-voltage curves resulting from simulated solar irradiation of nanotube cells annealed in air and ammonia, under AM1.5 (air mass 1.5) conditions.