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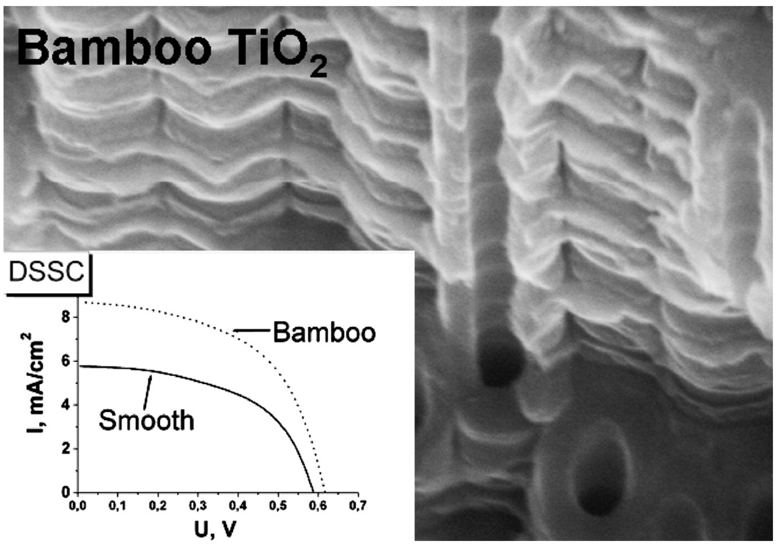

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Bamboo-Type TiO_2 Nanotubes: Improved Conversion Efficiency in Dye-Sensitized Solar Cells

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Since O'Regan and Grätzel reported on highly efficient TiO_2-based dye-sensitized solar cells (DSSCs),[1] many efforts are dedicated to enhance the light of these cells to electricity conversion efficiency. Recently, we replaced the conventional nanocrystalline TiO_2 particles (NPs) with self-organized TiO_2 nanotube layers (NTs), which provide considerably high surface area and a continuous cylindrical morphology.[2] More recently, Frank's group reported that the light−harvesting efficiencies of NT-based DSSCs were higher than those of NP-based DSSCs owing to stronger internal light-scattering effects.[3] Three key factors for efficient light harvesting and conversion are (i) the very high surface area of nanostructured oxide films for dye adsorption, (ii) efficient injection of electrons from excited dye to conduction band of TiO_2, and (iii) the transport of charge carriers through a porous structure that should take place with a minimized recombination loss of electrons.[4] A key advantage of self-aligned NT layers is that a defined nanoscale morphology of a high ordering is provided and can be controlled by the selection of the electrochemical conditions[5] (see also ref. 6 for an overview). The use of nanotubes for DSSCs provides a very high surface area with a 1D direction minimizing the number of detrimental grain boundaries one electron has to pass when traveling to the substrate. Several ways to improve the nanotube geometry toward higher conversion efficiency have been reported. Most recently it was shown that by reducing the disorder that is typically present at the top of the nanotube layers grown in nonaqueous electrolytes, an increase in the efficiency from 1.6% to 1.9% for AM 1.5 standard illumination can be reached.[3] In the present work, we show that a new generation of stratified TiO_2 nanotubes with a so-called bamboo type morphology[7] can substantially increase the conversion efficiency of NT-based DSSCs. Figure 1a schematically shows the different generations of solar cells−from the traditional Grätzel-type to the NT-based and the B-NT-based solar cells presented in this work.

Bamboo-type tubes as well as conventional smooth-walled tubes were prepared electrochemically by controlled anodization of Ti in an electrolyte consisting of 0.2 mol L^{-1} HF in ethylene glycol.[7] DC polarization lead to a dense array of aligned TiO_2 nanotubes as shown in scanning electron microscopy (Hitachi FE-SEM S4800) images of Figure 1b. Under these conditions the tube layer has a thickness of approximately 8 μm with an individual tube diameter of 120 nm. However, using appropriate alternating voltage cycling allows a switch between conditions that enable tube growth and conditions leading to a compact layer. Essentially, at each voltage step a compact connecting layer is formed in between the tubes and a bamboo type of structure can be grown (Figure 1c,d). Thus, by using different AV pulse durations the distance between the stratification layers can be adjusted. Figure 1panels c and d show two different bamboo morphologies used in this work with a spacing 70−370 nm and each grown to a layer thickness of 8 μm. The inset in Figure 1a shows that the tubes are indeed entirely opened on the inside between the bamboo rings.

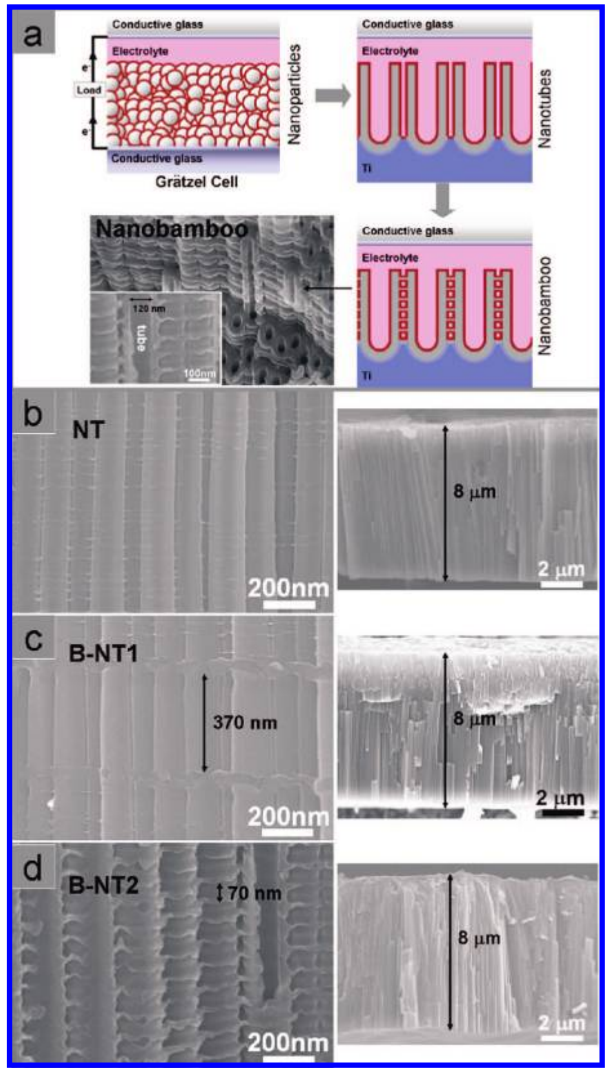

Figure 1. (a) Schematic representation of dye-sensitized TiO_2 solar cells, based on nanoparticle (NP), nanotube (NT), and bamboo type nanotube (B-NT). The inset shows a tilted SEM image of the nanobamboo morphology and a high magnification inset that shows the inner side of the B-NT structure to be open over the entire length. (b−d) SEM images of 8 μm thick TiO_2 layers: (b) smooth walled nanotube layers, grown under constant-voltage conditions at 120 V for 2 h; (c) bamboo-type tubes (B-NT1), grown under AV conditions, with a sequence of 5 min at 120 V and 5 min at 40 V for 4 h anodization; (d) bamboo-type tubes (B-NT2), grown under AV conditions, with a sequence of 1 min at 120 V and 5 min at 40 V for 12 h anodization. For panels b−d, images on the right show cross-sections for each sample.

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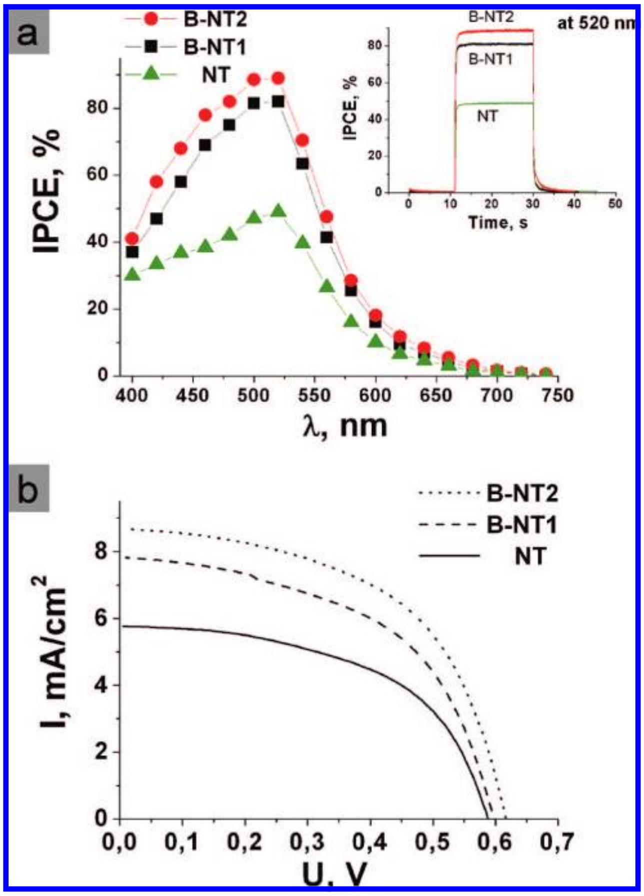

Figure 2. (a) IPCE values (incident phototo-photocurrent efficiency) and (b) I−V characteristics in a DSSCs configuration for the dye-sensitized TiO_2 nanotube layers shown in Figure 1: smooth (NT) and bamboo type (B-NT1 and B-NT2). The inset in panel a shows a photocurrent transient acquired at 520 nm wavelength.

The as−anodized self-organized TiO_2 nanotubes have an amorphous structure, which can be transformed to an anatase structure upon annealing in air at 450 °C (Supporting Information, Figure 1).[8] After annealing, all samples were dye-sensitized in Ru based dye. Incident photon-to-current conversion efficiency (IPCE) spectra are shown in Figure 2a. The inset shows typical photocurrent transients for the DSSCs; similar shapes of photocurrent transients were received in all experiments. The steady state value of the photocurrent transient was taken after 20 s of the light pulse. For the different layers the maximum $IPCE_{max}$ values result as 50% for the smooth NT, while the bamboo show significantly increased values of 82% (B-NT1) and 89% (B-NT2). Figure 2b shows the I−V characteristics for the DSSCs based on NT, B-NT1, and B-NT2, respectively. In line with IPCE results, the bamboo-type nanotubes-based DSSCs show a significantly higher efficiency than smooth-walled tubes as summarized in Table 1.

Table 1. Photovoltaic Characteristics of Dye-Sensitized NT, B-NT1 and B-NT2

	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)	L_{dye} (au)
NT	5.93	0.59	0.51	1.90	52
B-NT1	7.85	0.60	0.51	2.48	69
B-NT2	8.76	0.62	0.52	2.96	78

The present work shows that the solar conversion efficiency can be strongly enhanced by modulating TiO_2 nanotube morphology. IMPS and IMVS characterization of the carrier transport and recombination kinetics do not reveal a significant difference between the two morphologies (Figure SI 2). This indicates that although the stratification between the nanotubes in principle allow for a longer random walk path for photogenerated carriers, neither the transport properties nor the recombination kinetics are detrimentally affected by the bamboo structure. The key improvement provided by the bamboo structure is the higher dye loading per unit volume as evident from dye desorption measurements (L_{dye} (au)) included in Table 1. Not only can the additional area provided by the bamboo rings add to the active area but also the spacing introduced between the tubes may allow dye molecules to cover the interior and exterior of TiO_2 NT walls.[3]

In summary, the present work shows that TiO_2 nanobamboo tubes grown by alternating-voltage anodization of Ti in fluoride-containing electrolytes can enhance the photoconversion efficiency for nanotube based DSSCs. The structure presented here is far from being optimized but the work indicates that TiO_2 nanotube layers may become a potential substitute for classical nanoparticulate thin film layers as a photoanode in DSSCs. The present work also shows that by a simple variation of the electrochemical conditions, the geometry and surface properties of the nanotube layers can be altered over a wide range. Key to the higher efficiency is the substantial increase in dye loading of the material that can be achieved because of the bamboo rings.

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Supporting Information Available: Detailed experimental procedure, XRD crystallographic spectra, dye loading measurements, charge transport, and recombination dynamics measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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