ELECTRONIC SUPPLEMENTARY INFORMATION

Plasma assisted deposition of single and multistacked TiO_2 hierarchical nanotubes photoanodes

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Section S1.

Assembly of the solar cells.

Counter electrode. FTO/glass substrates of 2.5 x 2 cm^2 provided by Xop Glass (12-14 Ω/□) were drilled in two points for later electrolyte injection, rinsed with acetone, isopropanol and absolute ethanol and heated to 500 ºC for 1 hour. 12 uL of plastisol (Solaronix) were dispersed on the substrates, dried in air and heated in a furnace for 20' at 400 ºC.

Working electrodes. FTO/glass substrates were cleaned just as the counter electrodes. An active area of 0.7 cm^2 was defined with an aluminum foil mask and a layer of less than 200 nm of TiO_2 was deposited by PECVD acting as a hole blocking layer and providing the necessary roughness for the growth of ONWs. NTs with different thicknesses were fabricated by PECVD onto the FTO electrode through a mask to delimitate a covered area of 7 x 10 mm^2. Samples were heated up to 120 ºC before immersing overnight in the dye solution, 0.5 mM solution of N719 dye (cis-diisothiocyanato-bis(2,20-bipyridyl-4,40-dicarboxylato) ruthenium(II) bis (tetrabutylammonium)) [purchased from Solaronix] in ethanol, to prevent adsorption of air moisture. Polished n-type Si(100) purchased from Topsil and fused silica from Sico Technology GmbH were used in each preparation for later characterization.

Electrolytic solution. It was prepared by addition of 0.6 M 1,2-dimethyl-3-propylimidazole iodine (DMPII), 0.1 M LiI, 0.5M 4-tertbutyl-pyridine (TBP), 0.05 M I2 and 0.1 M guanidinium thiocyanate (GuSCN) to a mixture of acetonitrile/valeronitrile (85/15).

Sealing of the cells. A frame of a thermoplastic polymer (Surlyn, Solaronix) was placed on the perimeter of the active area and then sandwiched with the counterelectrode. The whole cell was heated to 140 ºC under slight pressure to ensure a proper sealing. After that the electrolyte was injected and the holes on the counterelectrode sealed with Surlyn and a cover slide glass.

Characterization of DSCs. The solar-cell devices were characterized using a solar simulator with an AM1.5G filter (ABET). A reference solar cell with temperature output (Oriel, 91150) was used for calibration. Electrochemical Impedance Spectroscopy (EIS) measurements were performed under light with perturbations in the 105-10-3 Hz range and the intensity-modulated photovoltage spectroscopy (IMPS) measurements in the same Hz range. For all the small perturbation techniques, a LED LUXEON collimated (540 nm) source and an Autolab/PGSTAT302N potentiostat were used. Zview equivalent circuit modelling software (Scribner) was used to fit the EIS data, including the distributed element DX11 (transmission line model). The NOVA 1.7 software was used to analyze the IMPS data.

Calculation of efficiency from IV characteristic curves.

The power conversion efficiency of a cell is generally defined as:

$$\eta = \frac{J_{SC} \times V_{OC} \times FF}{P_{sun}}$$

Where J_{SC} is the short-circuit photocurrent per unit of active area of the solar cell (mA/cm^2) and it represents the maximum attainable current flow at closed circuit (zero resistance). V_{OC} is the open-circuit photovoltage, achieved under no current flow conditions (infinite resistance). P_{sun} is the power of the incident light and *FF* stands for the fill factor of the cell, a parameter representing the ease of extraction of the photogenerated carriers out of the photovoltaic device. The *FF* is mathematically expressed as:

$$FF = \frac{J_{mp} \times V_{mp}}{J_{SC} \times V_{OC}}$$

$J_{mp} \times V_{mp} = P_{mp}$ is the maximum power output of the cell, while $J_{SC} \times V_{OC}$ is the so-called 'dummy' power output of the device.

In order to study the response of the solar cells, a standard spectral distribution of light corresponding to an Air Mass parameter of 1.5G (AM 1.5G) is normally used, but the irradiance is set to 1000 W/m^2.

Table S1. Mean HNT length obtained from statistics on cross-section SEM micrographs.

Sample	Mean length (μm)
660 nm	2.67 (extrapolated)
1.6 μm NT	3.14±1.26
6.6 μm NT	5.62±3.34

Table S2. Size of the crystallite determined by the Scherrer method after the XRD patterns in Figure 1 g) and S3, see also reference 19.

Sample	Crystallite size (nm) (101)
660 nm TF	49.1
1.6 μm TF	57.6
6.6 μm TF	72.7
660 nm HNT	42.9
1.6 μm HNT	39.1
6.6 μm HNT	86.6

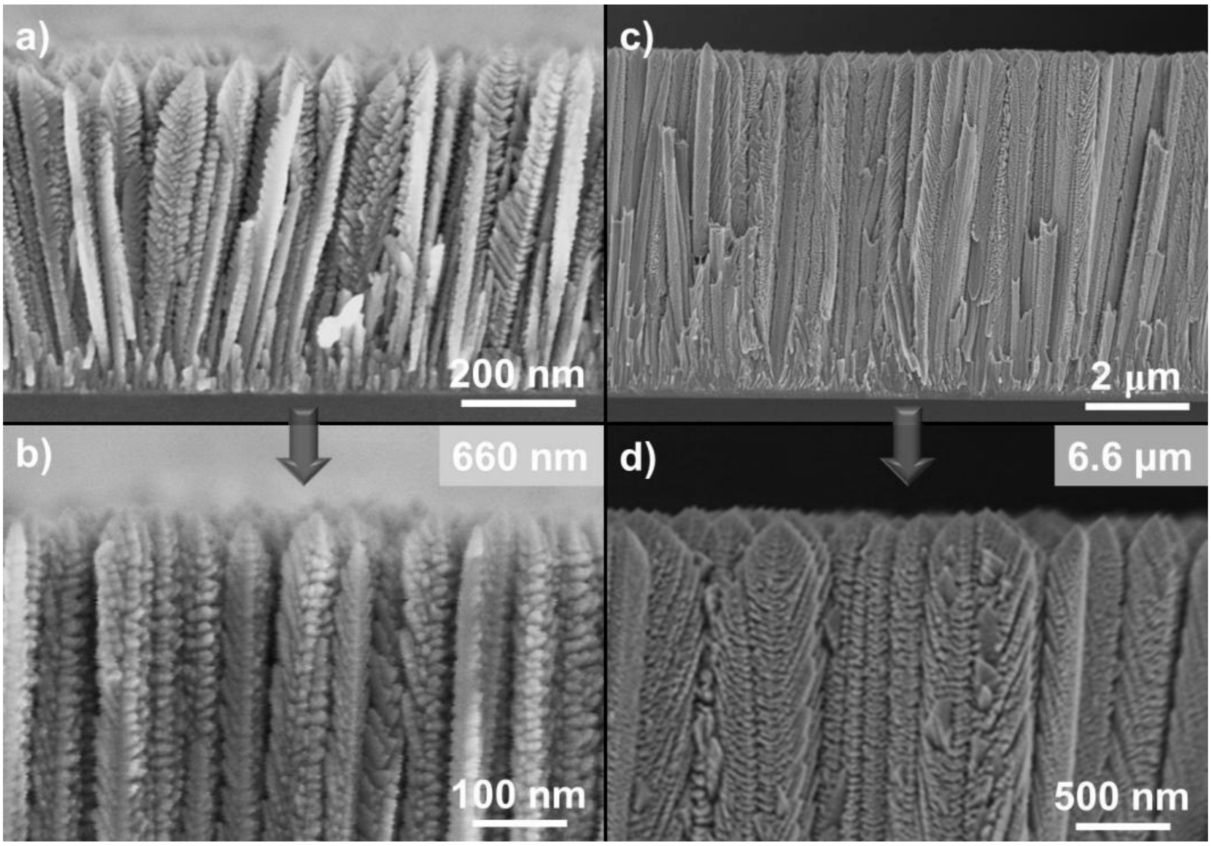

Figure S1. SEM cross sections of 660 nm (a-b) and 6.6 µm (c-d) anatase thin films. Some interesting changes are readily observed in anatase thin films used as reference when the thickness was increased ten times. The first noticeable difference is the interspacing between adjacent anatase columns. For 660 nm there exist clear gaps between columns (a)-b)), while for 6.6 µm the empty space has been drastically reduced, producing more closed-packed structures (c)-d)). Secondly, the size of the columns has evolved from less than 100 nm to more than 200-300 nm, which certainly explains the reduction of free space.

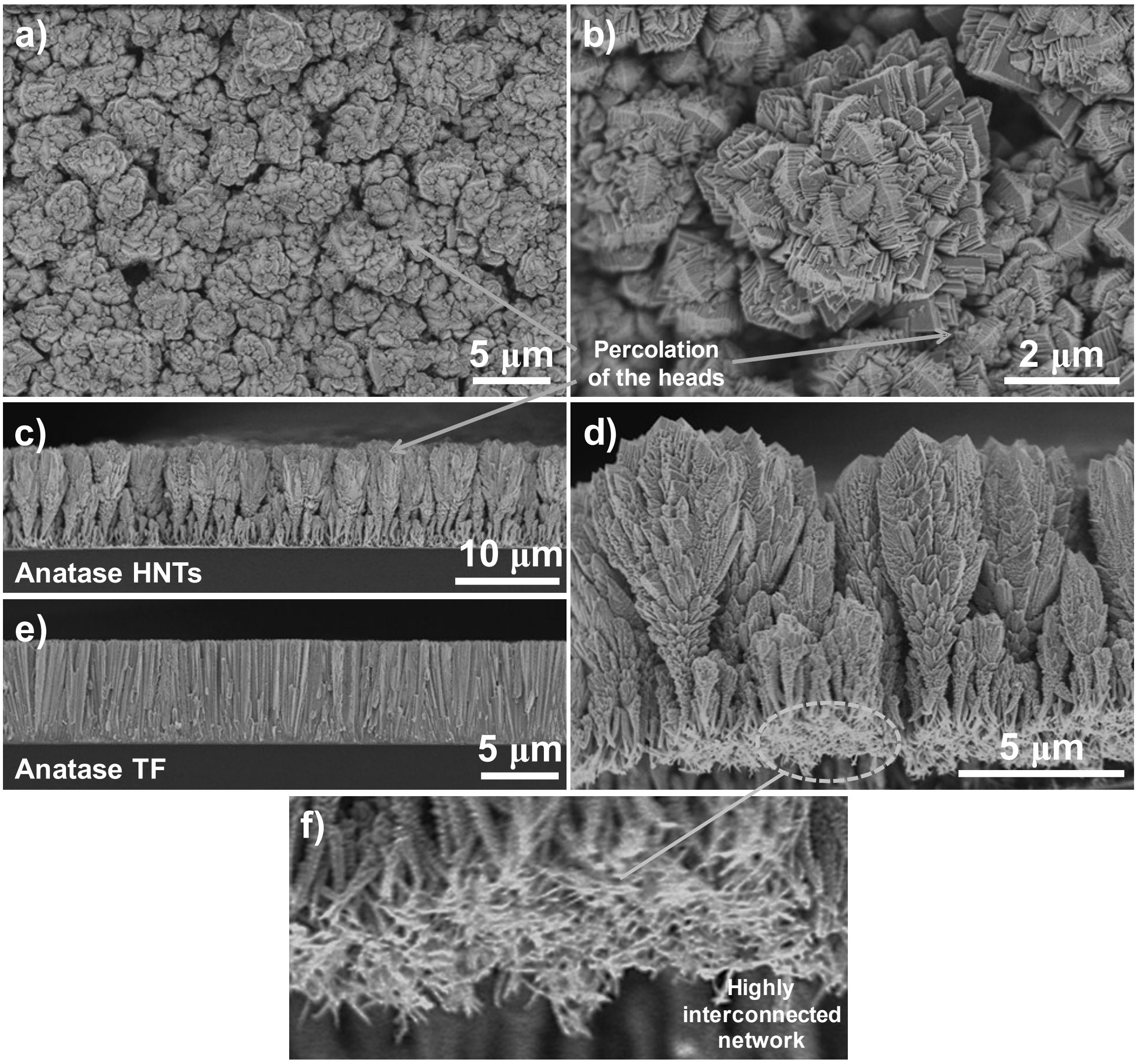

Figure S2. SEM images in normal view of 6.6 µm anatase HNTs (a) and (b). Cross sections of HNTs (c)-(d) and thin film (e). f) zoomed region in (d). Interconnection is visible in panel d), and more clear in panel f), where an island of these structures has detached from the substrate.

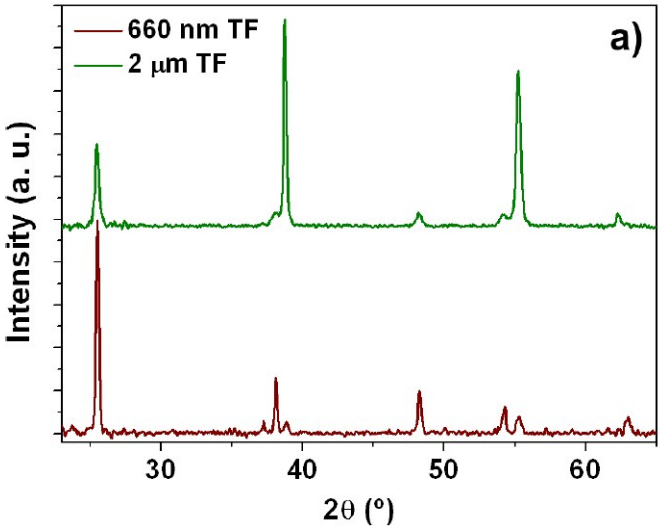

Figure S3. XRD diagrams of anatase TFs of 660 nm and 2 μm adapted from reference 19 in the main text.

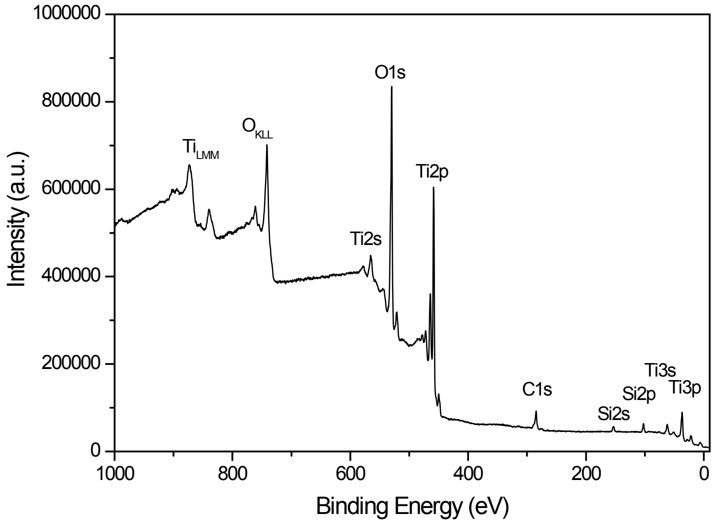

Figure S4. XPS survey spectrum acquired for 660 –HNTs deposited on a Si(100) wafer.

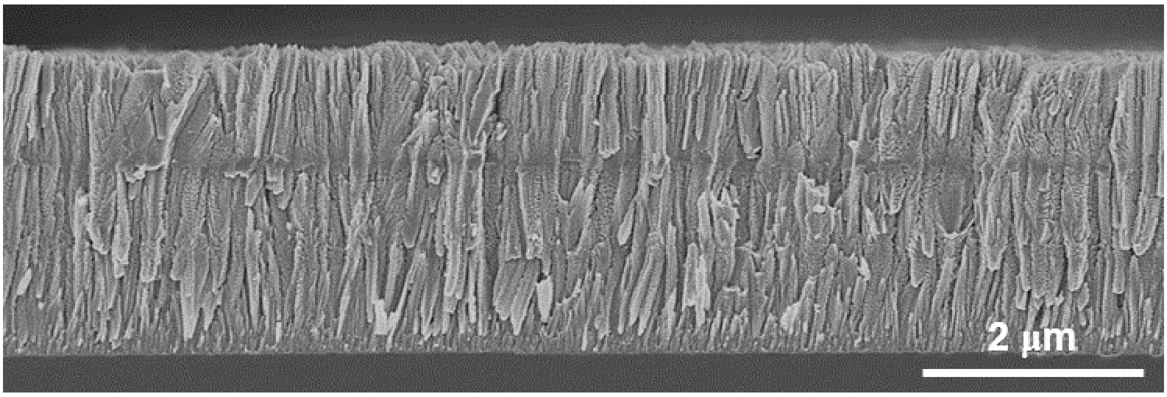

Figure S5. SEM cross section of the equivalent thin film for the stack in Figure 2 g).

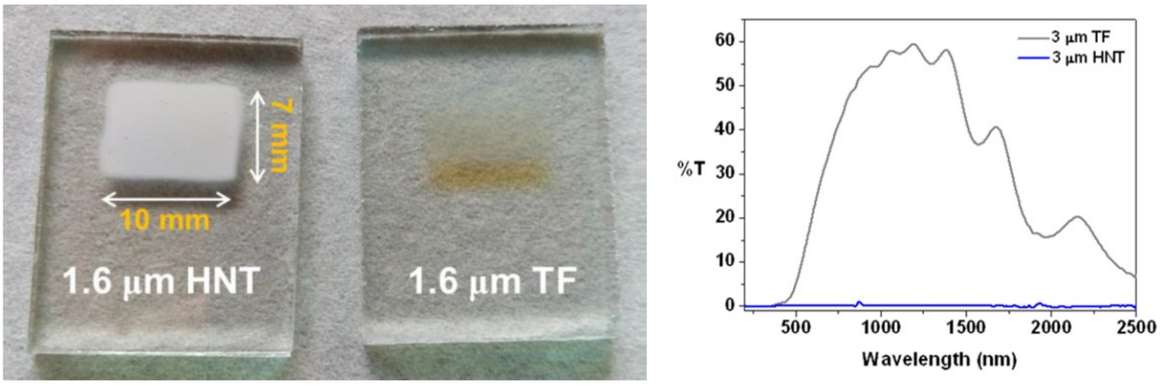

Figure S6. Photograph of 1.6 µm thick anatase thin film (right) and HNTs (left) samples prepared on FTO coated glass. UV-Vis-NIR transmission spectra of 3 µm thick anatase thin film and HNTs on FTO/glass.

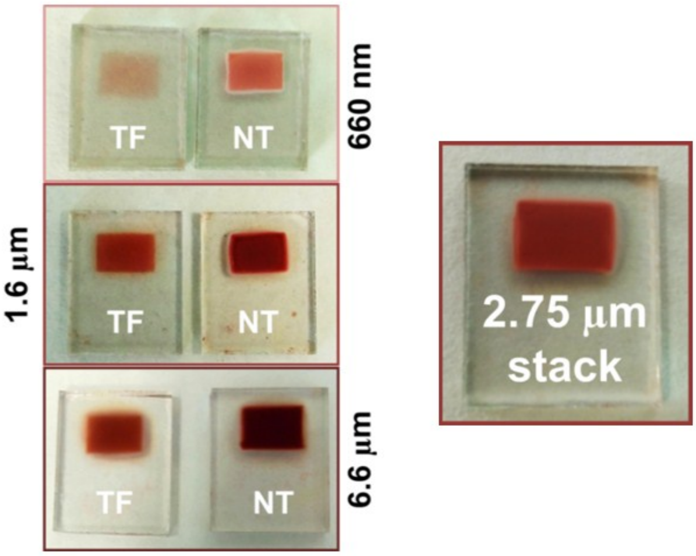

Figure S7. Photographs of DSCs electrodes after overnight immersion in dye N719 as labelled.

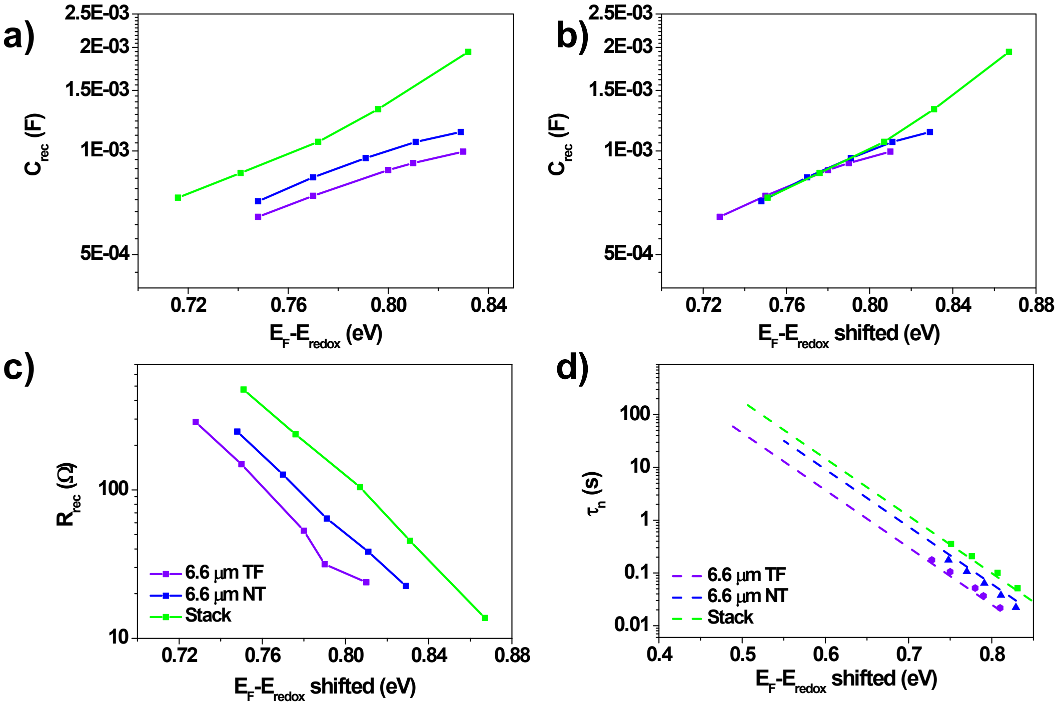

Figure S8. a-d) Impedance spectroscopy results of DSCs fabricated with 6.6 um anatase thin films and nanotubes, and the stack of NTs. (a) Recombination resistance extracted from the fitting of the Electrochemical Impedance Spectroscopy (EIS) spectra at various applied potentials. Impedance parameters plotted at various shifted potentials: b) Capacitance, c) Recombination resistance and d) Electron lifetime (symbols represent the calculated values and the dashes the extrapolated ones). The approach used by González-Pedro V. et al.[24] was followed in order to compare the recombination resistance and electron lifetime of the different samples at the same capacitance.

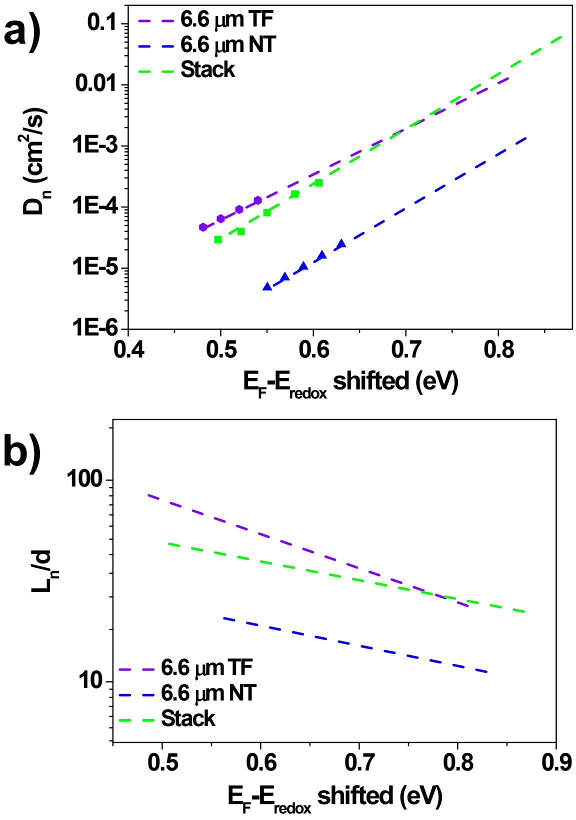

Figure S9. (a) Diffusion coefficient and (b) normalized diffusion length for DSCs with 6.6 µm anatase thin films and nanotubes, and the stack determined at various shifted potentials. The approach used by González-Pedro V. et al.[24] was followed in order to compare the diffusion coefficient and diffusion length of the different samples at the same capacitance.