Supporting Information

Hierarchical DSSC structures based on "single walled" TiO₂ nanotube arrays reach backside illumination solar light conversion efficiency of 8 %

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Figure S1.

(a) Schematic of a DSSC illustrated in a back-side configuration. (b) Overview of DSSC efficiencies in literature using TiO_2 nanotube layers in a back-side illumination configuration, compared with efficiency reached in the present work (red star); the insert shows schematically the de-coring / multiple layer decoration used in the present work.



* World-record efficiency of nanotube based front-side illumination DSSC is > 9 %, based on membrane transfer process on FTO with a thin layer of TiO₂ nanoparticle between the membrane and FTO.⁸ For completely anodized thin film Ti on FTO approaches, the best front-side efficiency is 6.9 % ⁹.

Figure S2

SEM and TEM images of double and single walled nanotubes taken at the top surface and near the nanotube bottoms after annealing at 450 °C.



Figure S3.

SEM images double walled tubes after 2 times decoration with TiO_2 nanoparticles. This illustrates the incompatibility of classic tubes with a controlled layer-by-layer decoration (due to less defined inner shell of this tube type).



Remnants not entering tubes

Clogged openings

Figure S4.

SEM and TEM images of single walled nanotube layers after 1 time $TiCl_4$ treatment. Additionally at the bottom of nanotube layers also TiO_2 nanoparticles can be found.



Figure S5.

XPS spectra taken on double walled and single walled nanotube samples after annealing at 150 °C and 450 °C. The results show that double walled nanotube samples have a high carbon content; after the core removal the single walled nanotube samples have a significantly lower carbon content.



Figure S6.

EDX analysis for carbon taken at 3 different locations of cross sections of single- and double walled nanotubes.







Figure S8. Comparison of (a) calculation are based on dye absorption using Beer lambert's law from the absorption spectra and (b) Kubelka-Munk value spectra calculated from diffuse reflectance measurements.



Here we compare dye loading by dissolving the dye from the TiO_2 nanotube samples using 10 mM KOH solution and then calculate dye absorption on the layers using the Beer Lambert's law (as frequently used in literature¹⁰) with measurements of the diffuse reflectance and convertion to absorption in the absorbance region of the dye (600nm). Both data show that double walled samples have higher amount of dye adsorbed. (This is because inner wall from the double walled nanotube after annealing gets rough and thus gives additional surface area for dye adsorption.) Both, single and double walled samples, when loading additional nanoparticle layers, also show an increase in the amount of dye adsorption, <u>**but**</u> the double walled TiO_2 nanotube layers (with more than 2 times nanoparticle decoration) start to clog openings and do not allow a defined layer by layer decoration. (see in figure S3)

Figure S9.

XRD spectra taken on double walled and single walled nanotube samples after annealing at 150 °C and 450 °C. The thermal treatment at 150 °C has no apparent effect on the crystallinity, after annealing at 450 °C conversion to anatase has occurred. (A = anatase, Ti = Titianium)



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