Inducing a nanotwinned grain structure within the TiO₂ nanotubes provides enhanced electron transport and DSSC efficiencies > 10 %

Seulgi So[‡], Imgon Hwang[‡], JeongEun Yoo, Shiva Mohajernia, Mirza Mačković, Erdmann Spiecker, Anca Mazare, Patrik Schmuki^{*}

[‡] Equal contributions

Dr. Seulgi So^{1,2}, Imgon Hwang¹, JeongEun Yoo¹, Shiva Mohajernia¹, Dr. Mirza Mačković³, Prof. Dr. Erdmann Spiecker³, Dr. Anca Mazare¹, Prof. Dr. Patrik Schmuki^{1,4,*}

¹Department of Materials Science and Engineering, WW4-LKO, University of Erlangen-Nuremberg, Martensstrasse 7, D-91058 Erlangen, Germany

²Department of Chemistry, University of California, Irvine, United States

³Department of Materials Science and Engineering, Institute of Micro- and Nanostructure Research and Center for Nanoanalysis and Electron Microscopy, Cauerstr 6, D-91058 Erlangen, Germany

⁴Chemistry Department, Faculty of Sciences, King Abdulaziz University, 80203 Jeddah, Saudi Arabia

Link to the published article:

<https://onlinelibrary.wiley.com/doi/full/10.1002/aenm.201800981>

Keywords: TiO₂ nanotubes, nanotwinned, conductivity, DSSCs

Titania is one of the key materials used in 1, 2 and 3D nanostructures as electron transport media in energy conversion devices. In the present work we show that the electronic properties of TiO₂ nanotubes can be drastically improved by inducing a nanotwinned grain structure in the nanotube wall. This structure can be exclusively induced for “single-walled” nanotubes with a high temperature treatment in pure oxygen atmospheres. Nanotubes with a twinned grain structure within the tube wall show a strongly enhanced conductivity and photogenerated charge transport compared to classic nanotubes. We exemplify this remarkable improvement in the electronic properties by using nanotwinned TiO₂ nanotubes in dye-sensitized solar cells where a significant increase in efficiency of up to 10.2% is achieved.

Since the discovery of 1-dimensional carbon nanotubes by Ijima in 1991,^[1] 1D structures have shown tremendous potential in a wide range of structural and functional applications. A key advantage of the 1-dimensional (1D) conductive or semiconductive geometry is that a drastically enhanced directional electron transport can be achieved.^[1-4] Meanwhile, not only carbon- or Si-based 1D structures but also a range of inorganic semiconductor materials such as ZnO or TiO₂ received wide interest as they can serve as an effective electron conducting scaffold in virtually any non-planar solar cell configuration such as Grätzel type dye sensitized cells (DSSC) or perovskite-based cells.^[5-8] Among various nanowire, nanorod or nanotube geometries, particularly self-organized TiO₂ nanotube layers have become intensively explored in a range of electrical or photoelectrochemical applications such as sensors, solar cells or photoreactors.^[3] These vertically aligned TiO₂ nanotubes can be directly grown on a Ti substrate by a self-organizing electrochemical anodization process that allows the control of the tube geometry (length, diameter, wall thickness) by adjusting the anodization conditions.^[4,9]

In constructing dye-sensitized solar cells (DSSCs), a key element is that photogenerated electrons (injected from an excited absorber molecule to the TiO_2 conduction band) have to travel through the TiO_2 scaffold to the back contact. In the classic Grätzel setting, ^[5] nanoparticle assemblies (sintered or compacted) are used as a scaffold for the transport of photoexcited electrons. In order to improve the electron transport properties, over the past ten years, photoanodes based on self-organized TiO_2 nanotube layers (instead of TiO_2 nanoparticulate layers) have been explored in “front-side” or “back-side” configuration solar cells. In spite of considerable success and a continuously improved processing towards more optimized cells, the electron mobility in such tubes was found to be disappointingly low, in some cases mobilities inferior even to TiO_2 layers formed by simple particle assemblies were reported. ^[10]

This has led to an increasing awareness that a key deficiency of anodic TiO_2 nanotubes (NTs) is their intrinsic oxide structure and composition. ^[10-12] More specifically, the electron transport in TiO_2 NTs was found to be generally limited by a high amount of lattice defects due to an oxygen deficient stoichiometry (TiO_{2-x}), as well as by impurities and grain boundaries in tube walls. ^[10,11] All these factors were reported to be causes for a low electron mobility and the origin of a high density of carrier recombination states. ^[10,11] Based on terahertz spectroscopy Richter et al. ^[10] assigned the low electron transport rates in TiO_2 nanotubes to exciton-like trap states. These states were ascribed to the sub stoichiometry in TiO_2 nanotubes. Other studies on the transport properties that were carried out on a single TiO_2 nanotube, i.e. a tube that was separated from an anodic TiO_2 nanotube layer and used in a four point setting along the tube, ^[11] led to the conclusion that in polycrystalline tubes defects in the grain cores rather than grain boundaries control the electronic transport via a Mott type hopping mechanism. ^[11]

In contrast to these works, ^[10,11] numerous experimental studies on thermal crystallization show a tremendous influence of annealing conditions on tube wall morphology and of the grain structure and the nature of grain boundaries on the macroscopic performance of TiO_2 nanotube

layers in photoelectrochemical applications. ^[11,13-15] Additionally from these works one can also extract that the electrical properties of nanotubes can significantly be improved by removing the most resistive part of tubes (*i.e.* their bottoms) ^[16], and by producing so called single-walled (SW) tubes that provide a significantly lower contamination level than conventional tubes. ^[17-19] Nevertheless, the tubes still consist of a classic crystal-grain and boundary structure that limits electron mobility and conductivity.

Herein, we report on a drastic improvement in electronic properties of TiO₂ nanotubes by inducing a modified grain structure within the nanotube wall, which is an anatase structure that consists of nanotwinned grains. This change from a classic grain structure to twinned grains, as illustrated in **Figure 1a-c** (the twins in Figure 1c are indicated by white arrows), leads to a two order of magnitude decrease in the electrical resistance (**Figure 1d**) and as a result to an strong increase in the performance if such tubes are used in DSSCs (**Figure 1e**, from 7.6% to 10.2%). Beneficial effects of twinned nanostructures on the electronic properties were reported particularly for metallic nanostructures (e.g. Cu nanowires) ^[20] and for II-VI semiconductor structures (e.g. ZnSe nanowires, ^[21-23] ternary chalcogenate (Cd_{0.5}Zn_{0.5}S) nanorods ^[24]). The main effects are ascribed to a local increase in mobility or carrier density, as carriers separation at the boundaries is favored due to the local lateral field between the grain boundaries and grain interiors or alternatively to strain relaxation at twin boundaries. ^[25] Beneficial effects are also ascribed to the formation of defined homojunctions due to twinning; these junctions were reported to be very efficient in separating photo-generated charges and contributing to prolonged lifetime of both photo-generated electrons and holes. ^[24]

The present work shows for the first time that thermal annealing of amorphous TiO₂ nanotubes under specific atmosphere conditions can lead to a crystalline anatase structure consisting of nanotwinned grains within the nanotube walls.

Figure 2 shows an overview of the thermal crystallization conditions studied in this work on different tube morphologies, namely single-walled (SW) or double-walled (DW) nanotubes.

Anodic nanotubes grown under most conditions are amorphous and have a double-walled structure.^[3,26] Single-walled nanotubes were obtained by a decoring process, i.e. a suitable annealing and etching process that removes the inner typically C-contamination layer – see SI. In the as-formed (amorphous) tubes, besides a high density of defects, the oxide is substoichiometric.^[11] Usually these tubes are converted to anatase in air at temperatures from 400 to 600 °C – this crystallization process is however accompanied with the formation of oxygen vacancies if carried out in ambient (air) atmosphere.^[11,16,27] For this reason, in the present work we used annealing in pure oxygen atmospheres.

In order to avoid substrate effects during annealing,^[28] and to be able to construct front and back side illuminated DSSCs, we fabricated free standing TiO₂ membranes by a lift-off process (**Figure S2, S3**).^[29,30] The membranes were then annealed in oxygen or air at 450, 550, 650 and 750 °C and subsequently transferred to FTO, as described in the SI. Typical morphologies of double-walled and single-walled nanotube membranes after annealing in air or oxygen atmosphere are shown in Figure 2, for temperatures of 450 and 650 °C. For the double-walled membranes, the outer and inner layers are clearly visible as a result of the thermal decomposition of carbon from the inner layer (Figure 2, insert; **Figure S4, S5**). Air annealing at 450 °C (A450) results in a larger grain size than at 650 °C. For single-walled tubes, for both 450 °C and 650 °C the grains are larger. In double-walled tubes for oxygen annealing at 650 °C (O650), the grains become even larger while the inner and outer wall fuse together. The HAADF-STEM images in Figure 2g,h reveal the internal structure of classic nanotubes (except SO650), which are composed of randomly oriented nanosized grains and exhibit a certain degree of porosity. Please note the relatively broad size range of the pores (dark contrasts visible in Figure 2g,h). Most remarkable, for the single-walled nanotube membranes (SM) annealed in pure oxygen at 650 °C, nanotwinned grains are observed, as shown in Figure 2j-l. While any annealing attempt of double-walled nanotubes could not induce a twinned structure for single walled tubes annealed in oxygen atmosphere at 650°C (SO650) Figure 2j,k show line contrasts

within the grains that reflects the presence of twins along entire tubes. HAADF-STEM imaging of such line contrast at higher resolution (see Figure 2l) clearly shows the nanotwinned grain structure on an atomic scale. It should be mentioned that such nanotwinned grains can be also observed from SEM in the tube walls, (SEM in Figure 2 and Figure S6).

Comparing the HRSTEM images of nanotubes with a classical and nanotwinned grain structure (i.e. DA450 – Figure 2i, and SO650 – Figure 2l), faceted grains are clearly observed in case of nanotubes containing nanotwinned grains (oxygen annealing at 650 °C). The nanotubes composed of a nanotwinned grain structure still show a pure anatase structure (see SAED pattern in Figure 2n).

In fact, XRD patterns in Figure 2m show that even after high temperature annealing, all membranes consist of pure anatase phase even up to 750 °C (see **Figure S7**). The single walled membrane (650 °C, pure oxygen) with the nanotwinned grains becomes entirely white (**Figure S9**), as a result of the eliminated carbon contamination and loss of color centers related to substoichiometric TiO_x .^[31-33] This is further confirmed by energy-dispersive X-ray spectroscopy (EDX, **Figure S10**), X-ray photoelectron spectroscopy (XPS, **Figure S11**) and electron paramagnetic resonance (EPR, **Figure S12**) measurement.

Most importantly, TiO_2 nanotubes with the nanotwinned grains show a strongly increased electrical conductivity in 4-point conductivity measurements (see Figure 1d, **Figure S1**). For example, the resistivity of these nanotubes is 94.1 Ωcm , i.e. almost two orders of magnitude lower than for classic double-walled (1198.6 Ωcm) or classic single-walled nanotubes (1062.2 Ωcm). In order to examine the effect of using nanotwinned anatase nanotubes instead of conventional anatase nanotubes in a photoelectrochemical application, we compared their performance in dye sensitized solar cells. Dye sensitized solar cells in back-side and front-side configurations were constructed as described in the SI (**Figure S13**). The IV characteristics for the different solar cells are compiled in Figure 1e and **Figure 3**.

When comparing the influence of temperature for air annealing, we observe that with increasing temperature from 450 °C to 650 °C (for both DW and SW membranes), the short-circuit current – J_{SC} , the open circuit voltage – V_{OC} , as well as the efficiency are improved (Figure 3a-c and **Figure S14**). The most notable factor is J_{SC} obtained from IV curves (and for reference from IPCE data, see **Figure S15**). In our previous work, we found that single-walled nanotubes typically provide for a lower dye loading but have a higher J_{SC} and a higher efficiency than double-walled nanotubes (annealed in air at 450 °C).^[17] Herein, the SW membranes annealed in air at 450 °C show an increase to 7.58% efficiency, from 7.12% for DW membranes (Figure 3a-c); this is due to the removal of the inner C-contamination rich layer in the SW nanotubes which leads to an improvement of the electronic properties. Moreover, with increasing the annealing temperature to 650 °C in air, the efficiency of both DW and SW membranes based DSSCs is increased; with both J_{SC} and V_{OC} being increased. In addition, annealing at 650 °C in air provides for tube walls with a higher dye loading compared to the 450 °C (i.e. for DW membranes from 158 to 180 nM/cm², and for SW membranes from 152 to 184 nM/cm²).

From these data (air vs oxygen, Figure 1e, 3 and **S16**), it is apparent that oxygen annealing (O650) improves the V_{OC} , as for the DW membrane the V_{OC} is over 0.85 V and more importantly for the generated nanotwinned grain structure from the SW membrane it reaches 0.9 V. In other words, the plain single-walled tube membrane with nanotwinned grains leads to a remarkably high DSSCs efficiency, of 9.4%, in spite of the comparably low dye loading. If the dye loading of the nanotwin-structured nanotube membrane is improved by a TiO₂ nanoparticle decoration, from 197 to 275 nM/cm² (see also **Figure S18, S19**), the DSSCs performance is further improved to an efficiency of 10.23%.

The origin of the improved V_{OC} for the nanotubes with the nanotwinned grain structure is directly related to improved electron recombination characteristics. Electron transfer and electron recombination time constants were obtained from intensity-modulated photocurrent spectroscopy (IMPS), intensity-modulated photovoltage spectroscopy (IMVS) and open circuit

voltage decay (OCVD) measurements. Electron transfer, recombination time and life time constant for the different membranes are given in **Figure 4a-c**. Clearly, the electron transport is significantly enhanced in the case of nanotubes containing nanotwinned grains, compared with the classic DW or SW membranes, and shows the fastest electron transfer of all structures. In general, by increasing the annealing temperature, the electron transfer times decrease (see Figure 4a,b). High temperature annealing of the membranes in air (A650) results in a shorter recombination time for both DW and SW membranes, due to the increased porosity and decreased grain size. For the tubes with the nanotwinned grains a slight effect on the electron recombination time is observed; however, in the OCVD measurements the TiO₂ membrane with nanotwinned grains shows a much slower V_{OC} decay (see Figure 4c), that is on overall, a much lower charge recombination in comparison to membranes with the classical grain structure. Random defects as well as grain boundaries are usually regarded as recombination centers, but after generating the nanotwinned grain structure in the nanotube wall, these defects are reduced as the twin boundary itself does not act as a recombination center.^[34] Additionally, for membranes containing nanotwinned grains (**Figure 4d**) IPCE spectra show a clearly higher photocurrent response than 450 or 650 °C air annealed (classic) membranes; moreover, when the tubes with the nanotwinned grains are further decorated with nanoparticles, an even higher photocurrent response over the entire wavelength region is obtained.

As for DSSCs a key element for good electronic characteristics is that photogenerated electrons, which are injected from an excited absorber molecule to the TiO₂ conduction band, have to travel through the TiO₂ scaffold to the back contact, we believe that in the case of nanotwinned nanotubes, the nanotwinned grain structure can promote the penetration of the charge carriers and thus facilitates their transport to the back contact of the solar cell (see also **Figure S20**). For the nucleation of sol-gel anatase nanoparticles Banfield et. al^[35] found characteristic {112} twin planes and concluded them to be a result of oriented attachment during crystallite nucleation and coarsening. The process is to a large extent controlled by impurities, defects and

affected by the growth kinetics.^[36,37] These observations are in general agreement with the present work but to which amount even further tuning of the nanotwinned structure can be achieved, and can be used to further enhance the overall device performance, needs to be investigated in upcoming work.

Nevertheless, the present work shows for the first time the formation of nanotwinned grain in the nanotube wall of TiO₂ nanotubes and their effect in drastically improving the electronic properties of TiO₂ nanotubes. It is noteworthy that such structures can only be induced for “single-walled” nanotubes annealed at sufficiently high temperatures in oxygen atmospheres. Similar treatments of classical nanotubes do not result in nanotwinned grains. The presence of nanotwins in single-walled nanotubes (either in the form of nanotube arrays or in the corresponding membranes) result in a more efficient charge transfer via suppressing scattering of electrons at grain boundaries and hence inhibiting the free charges’ recombination. Such nanotwinned structures are especially beneficial in photoelectrochemical applications, for example as for DSSCs based on hierarchical structures constructed with twinned TiO₂ nanotubes over 10.2% efficiency was achieved.

Experimental Section

TiO₂ nanotubes growth and subsequent conversion to membranes

As substrates for any type of TiO₂ nanotube growth we used titanium foils (99.6% purity, Goodfellow) with a thickness of 0.125 mm. Prior to tube formation the foils were cleaned by sonication in acetone and ethanol followed by rinsing with deionized (DI) water and drying in a nitrogen stream. To grow the anodic TiO₂ nanotube, the foils were anodized in a two electrode configuration with a counter electrode made from platinum gauze. The typical electrolyte for the growth of the TiO₂ nanotubes was 1.5 M lactic acid (LA, DL Lactic acid, ~90%, Fluka), 0.1 M ammonium fluoride (NH₄F) and 5 wt.% deionized H₂O in ethylene glycol (99 vol.%), held at a temperature of 60 °C at an applied potential of 120 V for 1 min 30 s. Single-walled TiO₂ nanotubes can be obtained from as-grown TiO₂ nanotubes by following procedure: the as-formed nanotube are annealed at 150 °C for 1 h in air, with a heating and cooling rate of 30 °C/min using a Rapid Thermal Annealer (Jipelec JetFirst100). Afterwards, the annealed nanotubes are etched by piranha solution (1:3 vol.% of H₂O₂/H₂SO₄) at 70 °C for 330 s. The conversion of the nanotubular layers to membranes is achieved by growing a second amorphous short-length nanotube layer underneath, which is later removed by immersion in H₂O₂ (for further details Figure S2, S3 for an example of single-walled membranes).

Annealing

The single-wall or double-wall nanotube membranes were annealed for 1h, in the temperature range from 450 °C to 750 °C in air or in oxygen atmosphere. To note that during annealing, membranes were place in between quartz glass slides

Dye sensitized solar cells (DSSCs)

In general, most DSSCs based on TiO₂ nanotubes use the Ti substrate as a direct back-contact, i.e. “back-side illumination”; however, due to losses in light, “front-side illumination” approaches were also investigated. This implies either anodization of thin Ti films deposited on FTO (direct and complete anodization) ^[38] or membrane transfer (TiO₂ nanotube layers are detached from the metal and placed on a FTO substrate) ^[27,39].

To use front-side illumination, the annealed membranes were transferred on FTO slides (7 Ω m⁻²) that were previously coated with ca. 1.5 μ m thick TiO₂ nanoparticle film (Ti-Nanoxide HT, Solaronix) deposited by a doctor-blade method. After drying in air for 2h, the samples were annealed at 450 °C for 1 h in air, with a heating and cooling rate of 10 °C/min using a Rapid Thermal Annealer (Jipelec JetFirst100).

For dye-sensitization, a Ru-based dye (cis-bis(isothiocyanato)bis(2,2-bipyridyl 4,4-dicarboxylato)ruthenium(II)bis-tetrabutylammonium) (D719, Everlight, Taiwan, same as the commonly called N719 dye) was used. Samples were dye-sensitized by immersing for 1 day in a 300 mM solution of the Ru-based dye in a mixture of acetonitrile and tert-butyl alcohol (volume ratio: 1:1). After dye-sensitization, the samples were rinsed with acetonitrile to remove the non-chemisorbed dye. To evaluate the photovoltaic performance, the sensitized nanotubes were sandwiched together with a Pt coated fluorine-doped glass counter electrode (TCO22-15, Solaronix) using a polymer adhesive spacer (Surlyn, Dupont). An electrolyte (0.60 M BMIM-I, 0.03 M I₂, 0.10 M GTC in acetonitrile/valeronitril (85:15 vol.%)/SB-163, IoLiTec Inc, Germany) was introduced into the space between the sandwiched cells. Using front-side illumination, the current–voltage characteristics of the cells were measured under simulated AM 1.5 illumination provided by a solar simulator (300 W Xe with an optical filter, Solarlight), applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2420 digital source meter. The active area was determined by the opening of the black shadow film mask to be 0.2 cm².

For the TiCl_4 -treatment, the TiO_2 nanotubes were immersed once or twice in 0.1 M TiCl_4 solution at 70 °C for 30 min. All treated samples were washed with DI water and ethanol, and then dried in nitrogen stream. After the TiCl_4 treatment, samples were annealed again; this second annealing step was performed at 450 °C for 10 min.

Characterization

A field-emission scanning electron microscope (FE-SEM, Hitachi SEM FE 4800) coupled with EDX and a transmission electron microscopy were used to characterize the morphology and nanostructure of the nanotubular samples. Transmission electron microscopy (TEM) was performed with a Titan³ Themis 300, a Phillips CM300 UltraTWIN and a Philips CM30 TWIN/STEM (FEI Company, Netherlands). The Titan³ Themis 300 is equipped with a high-brightness field-emission gun (X-FEG), a monochromator system (energy resolution 0.2 eV), two C_s -correctors (probe and image side) from CEOS (Corrected Electron Optical Systems GmbH), a high-angle annular dark-field (HAADF) detector and a 4k CMOS camera. This microscope was operated at 300 kV acceleration voltage. The Philips CM300 UltraTWIN and the CM30 TWIN/STEM microscopes are equipped with LaB_6 filaments, 2k and 1k charged coupled device cameras from TVIPS (Germany), respectively, and were operated at 300 kV acceleration voltage. For TEM analysis the TiO_2 nanotubes are prepared on commonly used copper TEM grids coated with a holey carbon film. During TEM analysis no noticeable electron-beam-induced damage was observed. The free available software ImageJ (version 1.48r) and the commercially available software DigitalMicrographTM were used for image analysis. The evaluation of the electron diffraction patterns was performed using the software JEMS^c (version 3.8431U2012) and the inorganic crystal structure database (ICSD). The structure and crystallinity of prepared samples were investigated by x-ray diffraction analysis (XRD, X'pert Philips PMD with a Panalytical X'celerator detector) using graphite-monochromatized $\text{CuK}\alpha$ radiation ($\lambda=1.54056$ Å). The composition and chemical state were

characterized by X-ray photoelectron spectroscopy (XPS, PHI 5600, US), and peaks were shifted to C1s at 284.8eV (peak fitting was performed in Multipak software). EPR spectra were recorded on a JEOL continuous wave spectrometer JES-FA200 equipped with an X-band Gunn oscillator bridge, a cylindrical mode cavity, and a helium cryostat. The samples were measured in the solid state in an air atmosphere in quartz EPR tubes with a similar loading of ≈ 0.05 mg. Background spectra were obtained on empty tubes at the same measurement conditions. The spectra shown were measured with the following parameters: Temperature 95 K, microwave frequency 8.960 GHz, modulation width 1.0 mT, microwave power 1.0 mW, modulation frequency 100 MHz, and time constant 0.1 s.

Incident photon-to-current conversion efficiency (IPCE) of DSSCs was performed with a 150W Xe arc lamp (LOT-Oriel Instruments) with an Oriel Cornerstone 74001/8m monochromator. The range of photocurrent spectra were recorded from 400 to 800 nm.

Intensity modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) measurements were carried out using a Zahner IM6 (Zahner Elektrik, Kronach, Germany) with an UV modulated light ($\lambda=365$ nm). The photoelectrochemical performance of the samples was analysed in pure 0.1 M Na₂SO₄ solution in a three-electrode configuration, consisting of TiO₂ nanotubes as a photoanode, platinum wire as a counter electrode and a Ag/AgCl (3 M NaCl) electrode as reference.

The range of frequency was modulated from 1 MHz to 1 kHz. In the open-circuit voltage (V_{OC}) decay (OCVD) measurement, the cell is first illuminated, and then the light is switched off. The decrease in V_{OC} during relaxation from the illuminated steady-state to the dark equilibrium is monitored.

Acknowledgements

M.M. and E.S. thank the German Research Foundation (DFG) for financial support through the Cluster of Excellence EXC315 “Engineering of Advanced Materials” (EAM) and the research training group GRK 1896 “In situ microscopy with electrons, X-rays and scanning probes”. S.S, I.H, J.Y, S.M., A.M and P.S acknowledge ERC (project ID: 340511).

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Figure 1. (a) Schematic overview including obtaining of nanotubes (NTs), conversion to membranes, annealing and transfer to FTO for classic and twin nanotubes. High resolution scanning transmission electron microscopy (HRSTEM) images of (b) classic and (c) nanotwinned nanotubes. (d) 4-point I-V curves of double-walled, single-walled and nanotwinned NT (see Figure S1). (e) I-V characteristics for DSSCs fabricated using different nanotube samples (double walled, single walled NT/annealed at 450 °C in air and nanotwinned structure (with and without optimized nanoparticle decorations/annealed at 650 °C in oxygen) and illumination configurations (back and front-side).

Figure 2. SEM images of double-walled nanotube (a,b,c) and single-walled nanotube (d,e,f) membranes after annealing in different temperature (450, 650 °C)/ atmosphere (air or oxygen). (insert: inside SEM images – please see in detail in Figure S4). STEM images of (g-i) classic nanotubes (except SO650) and (j-l) nanotwinned nanotubes (SO650). In l) the twin boundaries (TB) and the spacing between (101) lattice planes is indicated (m) XRD spectra of double-walled nanotubes (DA450, DA650, DO650) and single-walled nanotubes (SA450, SA650, SO650) after annealing at different temperatures (450, 650 °C)/ atmosphere (air or oxygen). (n) Selected area electron diffraction (SAED) pattern of SO650. (DM = double-walled nanotube membrane; SM = single-walled nanotube membrane; A450 = Air 450 °C; A650 = air 650 °C; O650 = oxy 650 °C)

Figure 3 I-V characteristics for DSSCs fabricated using (a) double walled (b) single walled TiO₂ nanotube membrane samples with different annealing conditions. (c) DSSCs efficiency table. (NP = only nanoparticle layer ($\approx 1.5 \mu\text{m}$); J_{sc} = short circuit current; V_{oc} = open circuit voltage; FF = fill factor; and η = efficiency)

Figure 4 (a) Electron transfer time (τ_e) constants from IMPS measurements and (b) Electron recombination time (τ_r) constants from IMVS measurements. (c) The electron life time derived from open circuit voltage decay (inset) in corresponding DSSCs as a function of V_{oc} . (d) IPCE spectra of the DSSCs with the single-walled TiO_2 membranes annealed in different conditions, and with and without TiO_2 nanoparticle decoration.