Supporting information for

**TiO$_2$ nanotubes with laterally spaced ordering enable optimized hierarchical structures with significantly enhanced photocatalytic H$_2$ generation**

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**Experimental section**

*Growth of TiO$_2$ nanotubes:* Titanium foils (Advent Research Materials, 0.125 mm thickness, 99.6+% purity) were degreased by sonication in acetone, ethanol and deionized water, followed by drying in N$_2$ gas stream. The TiO$_2$ nanotubes (NTs) were formed by anodizing titanium foils in triethylene glycol (TEG) electrolyte containing 0.3 M NH$_4$F and 3 M H$_2$O at 60 V for 2 h at 60 °C. The DC potential was applied by using a VLP 2403 pro, Volthcraft power supply. After the anodization, the samples were soaked in ethanol for few hours, and then dried under N$_2$ gas stream. Subsequently, the TiO$_2$ nanotubes were annealed at 450 °C in air for 1 h using a Rapid Thermal Annealer (Jipelec Jetfirst 100 RTA), with a heating and cooling rate of 30 °C min$^{-1}$. For reference TiO$_2$ NTs, titanium foils were anodized in ethylene glycol (EG) electrolyte containing 0.15 M NH$_4$F and 3 wt% H$_2$O, at 60 V for 15 min. The R-NTs were then annealed in air at 150°C for 1 h, followed by piranha treatment at 75°C for 2.5 min to increase inner diameter of the NTs. All piranha-treated samples were annealed in air at 450°C for 1 h.
**TiO₂ nanoparticle decoration:** For TiCl₄ treatments, aqueous solution of 0.1 M TiCl₄ was prepared under ice-cooled conditions. The TiO₂ nanotube layers were then treated in a closed vessel containing of 7 mL TiCl₄ solution at 70 ºC for 30 min. Subsequently, the samples were washed with distilled water and rinsed with ethanol to remove any excess TiCl₄, and finally dried in a N₂ stream; and this process was replicated many times. After this treatment, the decorated samples were annealed again at 450 ºC for 10 min (Rapid Thermal Annealer) to crystallize the attached nanoparticles.

**TiO₂ nanoparticle layers:** TiO₂ nanoparticle layers (Ti-nanoxide HT, Solaronix) were prepared by doctor blading method on fluorine-doped tin oxide glass (FTO).

**Pt nanoparticle decoration:** In order to decorate the TiO₂ NTs, plasma sputter deposition (EM SCD500, Leica) was used to deposit different amounts of Pt. The amount of Pt was controlled by measuring their nominal thickness with an automated quartz crystal film-thickness monitor.

**Characterization of the structure:** Field-emission scanning electron microscope (FE-SEM, Hitachi S4800) was used to characterize the morphology of the samples. The chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5600, US). X-ray diffraction (XRD) performed with a X’pert Philips MPD (equipped with a Panalytical X’celerator detector) using graphite monochromized Cu Kα radiation (λ = 1.54056 Å), was employed to examine the crystallographic properties of the materials. The fluorescence intensity was measured by a using a Newport Optical Power Meter at 425 nm. The hydroxyl radicals (•OH) detection was conducted by illumination of UV light (325 nm) on the samples immersed in aqueous solution of 3 mM terephthalic acid, 0.01 M NaOH and 0.1 M NaCl.

**Photocatalytic measurements:** Photocatalytic measurements were carried out by irradiating the TiO₂ nanotube films with UV light (HeCd laser, Kimmon, Japan; λ = 325 nm, expanded
beam size = 0.785 cm$^2$, nominal power of 23 mW cm$^{-2}$) in a 20 vol% ethanol-water solution (for 2 h) in a quartz tube. The amount of generated H$_2$ (which accumulated over time within the quartz tube) was measured by using a gas chromatograph (GCMS-QO2010SE, Shimadzu) equipped with a thermal conductivity detector and a Restek micropacked Shin Carbon ST column (2 m x 0.53 mm). Before the photocatalytic experiments, the reactor and the water-ethanol mixtures were purged with N$_2$ gas for 30 min to remove O$_2$.

**Photoelectrochemical measurements:** Photocurrent spectra were conducted in 0.1 M Na$_2$SO$_4$ under an applied potential of 0.5 V (vs. Ag/AgCl) in a three-electrode system using 150 W Xe-lamp (Oriel 6365) equipped with a Oriel Cornerstone 7400 1/8 m monochromator (illuminated area=0.785 cm$^2$).

**IMPS measurements:** Intensity modulated photocurrent spectroscopy (IMPS) measurements were conducted using modulated light (10% modulation depth) from a high power LED ($\lambda = 369$ nm). The modulation frequency was managed by a frequency response analyzer (FRA, Zahner IM6). The photocurrent of the cell was determined using an electrochemical interface (Zahner IM6), and fed back into FRA for analysis. The measurements were conducted in a three-electrode system: TiO$_2$ nanotube sample as a photoanode with an exposure area of 0.5 cm$^2$, a Pt wire as a counter electrode and an Ag/AgCl (3 M KCl) as a reference electrode. The potential of the samples was set to 0 V during the measurements to guarantee the photogenerated electrons are ejected to the back contact of titanium substrate. The electrochemical impedance (Nyquist plot) was measured under modulated light. The relevant measured parameter is the angular frequency ($\omega_{min}$) at which the imaginary IMPS shows the minimum value. The corresponding electron transport time ($\tau_t$) constant was assessed according to this equation: 

$$\tau_t = \frac{1}{\omega_{min}}$$

**Dye loading measurements:** Dye adsorption was conducted by immersing the samples in a 300 mM solution of Ru-based dye (cis-bis (isothiocyanato) bis(2,2-bipyridyl 4,4-
dicarboxylato) ruthenium(II) bistetrabutylam-monium) at 40°C for 1 day. The dye solution was a mixture of tert-butyl alcohol and acetonitrile. Subsequently, the samples were rinsed with ethanol to remove non-chemisorbed dye. Then the samples were soaked in an aqueous solution of 5 mL KOH (10 mM) for 30 min. The concentration of desorbed dye was measured spectroscopically (by using a Lambda XLS UV/VIS spectrophotometer, PerkinElmer) at $\lambda = 502$ nm.

References

Figure S1. a) SEM image of spaced TiO$_2$ nanotubes near the bottom and b) region of nanotubular existence for ethylene glycol based electrolytes as a function of applied voltage and water content (taken from ref. [25]).

Figure S2. SEM images of different intertube distances formed by anodization of titanium in diethylene glycol based electrolyte.
Figure S3. Bandgap evaluation determined from IPCE measurements, for compact oxide and spaced TiO$_2$ NTs with different intertube distances.

Figure S4. SEM images of a) top and b) cross-section of spaced TiO$_2$ NTs. The tube growth mechanism here is that spacing results from the initial TiO$_2$ NTs growth, where a selection mechanism similar to small nanotubes suppression in the case of conventional TiO$_2$ NTs layers occurs.
Figure S5. SEM images of a) reference TiO$_2$ NTs grown in EG based electrolyte at 60 V for 15 min and b) spaced TiO$_2$ NTs grown in TEG based electrolyte at 60 V for 2 h. Clearly the NTs grown in TEG have more spacing between tubes in comparison to conventional close-packed NTs.

Figure S6. SEM images of a) top surface and b) cross-sectional of TiO$_2$ nanoparticle layers prepared by doctor blading method on fluorine-doped tin oxide (FTO).
**Figure S7.** SEM image of reference TiO$_2$ NTs decorated with 2 layers of nanoparticles: already after 2 times completely filled in a not fully defined structure. Photocatalytic H$_2$ generation of this sample showed only half of that measure for spaced NTs (with 2 times decoration of nanoparticles).

**Figure S8.** Different thicknesses of spaced TiO$_2$ NTs decorated with 3 layers of TiO$_2$ nanoparticles and 1 nm-thick Pt layers: a) 1, b) 3, c) 5, d) 7 and e) 9 µm.
Figure S9. Photocatalytic H$_2$ evolution measured for spaced TiO$_2$ NTs after decoration with 3 layers of TiO$_2$ nanoparticles and different amounts of Pt. Clearly, 1-nm thick Pt layer led to a maximized photocatalytic H$_2$ generation. Larger amounts of Pt induced larger shading effect of TiO$_2$; this means the light absorption of TiO$_2$ was hindered because Pt covered the oxide surface.

Figure S10. XPS survey of TiO$_2$ NTs, and TiO$_2$ NTs decorated with TiO$_2$ nanoparticles and 10 nm-thick Pt layer. The successful deposition of Pt is confirmed by the appearance of signals peaking at 72, 315, and 332 eV in the XPS spectra, which correspond to the binding energies of Pt 4f, Pt 4d5 and 4d3, respectively.
Figure S11. Photocatalytic H₂ evolution rate measured for spaced TiO₂ NTs after decoration with 3 layers of nanoparticles and 1 nm thick Pt.