

Supplementary Information

Photocatalytic methane decomposition over vertically aligned transparent TiO₂ nanotube arrays

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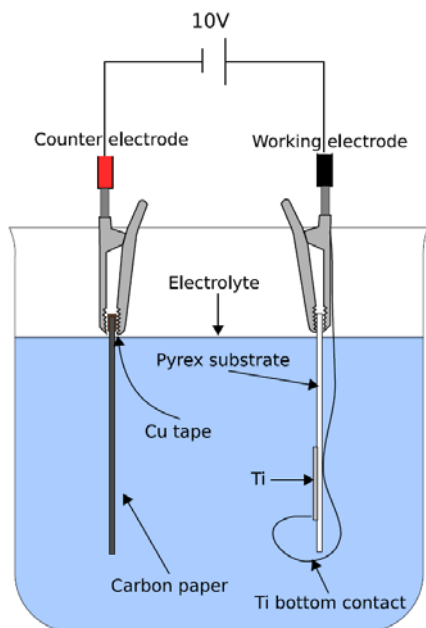


Figure S1. Schematic of the anodization procedure of the Ti film to produce VATNTs.

Field emission electron microscopy (FESEM)

A QUANTA 200 FEG MKII field emission scanning electron microscope (FESEM) was used at CEN, DTU. The procedure used for the SEM images was to connect the sample to the metallic sample holder by painting it with conductive silver paint. Secondly, a 3 nm layer of gold was sputter deposited on top by plasma sputtering. Figure S2 shows SEM images of the VATNTs on the Pyrex.

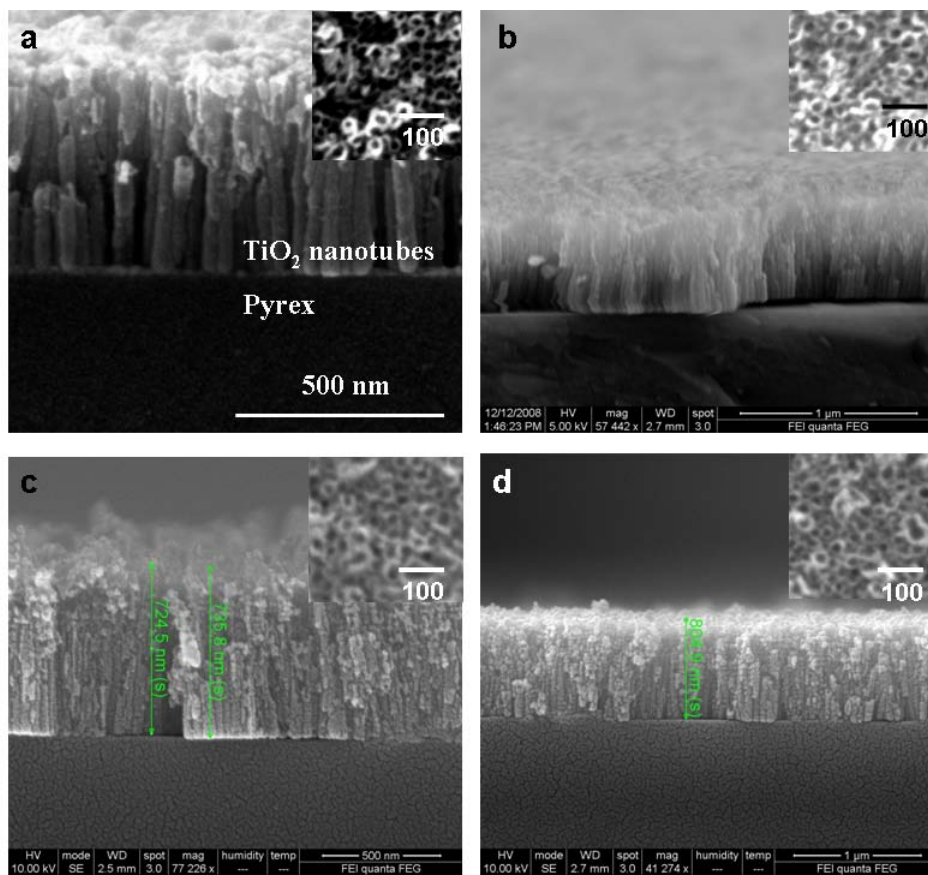


Figure S2. Representative cross-sectional FESEM images of (a) 450(400) nm, (b) 540(600) nm, (c) 730(800) nm and (d) 804(1000) nm thickness (Number in the parenthesis is the original Ti thickness). Insets show top-view images.

Transmission electron microscopy (TEM)

For the TEM investigation, the TNT array was scraped off from the Pyrex lid using a sharp scalpel, and put into a solution of pure ethanol to disperse the scrapings. The solution was sonicated for 10 minutes before dropping the solution on the carbon membrane. The TEM used for the investigation was a Tecnai T20 from FEI equipped with a thermionic filament.

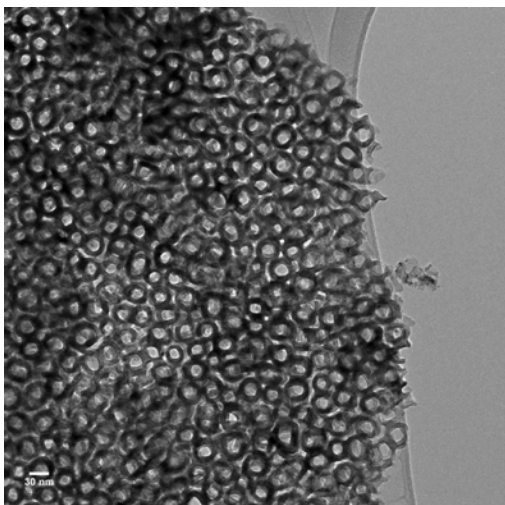


Figure S3. TEM top view image of 450 nm thickness VATNTs

X-ray diffraction (XRD)

The crystallinity of the VATNTs was investigated using a Philips X'pert Pro operating with copper radiation ($\text{Cu K}\alpha$) filtered with a nickel foil. Figure S4 shows a segment of the XRD spectra for the samples of varying thickness. For all of the spectra, a peak appears at 25° . This is the only resolvable visible peak that can be assigned to phases of TiO_2 , and therefore only this segment has been shown in the figure. The peak is assigned to the (101) planes of anatase (A) phase.

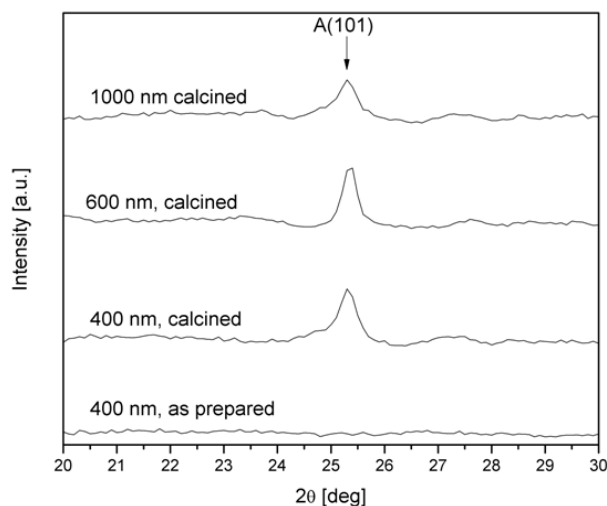


Figure S4. X-ray diffraction patterns of the VATNTs.

X-ray photoelectron spectroscopy (XPS)

X-ray photoemission spectroscopy (XPS) (Figure S5) was used to investigate Ti 2p and O 2p core levels of the VATNTs. For all the XPS data obtained, the Al K α peak at 1486.68 eV was used to probe the sample. An acceleration voltage of 15000 V, a current of 0.0067 A, and a pass energy of 50 eV was used. There is no signal attributed to metallic Ti, as evidenced by the lack of signal at around 454 eV. The Ti 2p region of the samples has binding energies (BEs) of 459 eV and 464.7 eV, attributed to the spin-orbit split (2p $_{3/2}$ and 2p $_{1/2}$) of the 2p core level. XPS results suggest that fully oxidized VATNTs were successfully produced.

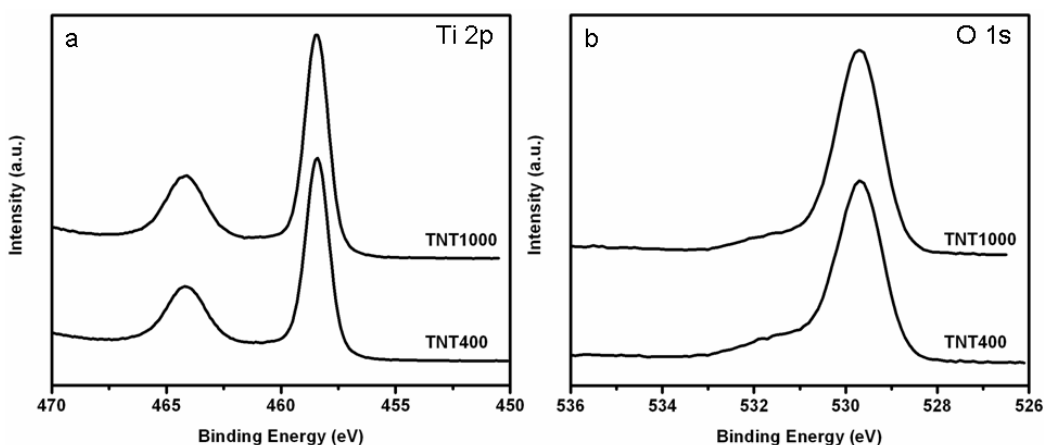


Figure S5. (a) Ti 2p XP spectra of the samples. (b) O 1s XP spectra of the samples.

The light source is a high intensity Hamamatsu UV-LED (model LC-L2) with a peak intensity at 367 nm \pm 10nm at FWHM (the irradiance spectrum is shown in Figure S6), and therefore the light from this source fits well with the band edge of TiO $_2$. The LED is fitted with a focusing lens (Hamamatsu L10561-220), which at 1 cm distance ensures an 8 mm diameter light spot, making it well suited for the purpose of illuminating samples in the μ -reactor. The spectrum was measured with a spectroradiometer (International Light model RPS-900R) at a distance of 1 cm, using a ND (Neutral Density) filter (Newport Co.) with an absorbance of approximately 2.0 in front of the LED in order to avoid the signal saturation. The LED can be coupled to a computer via USB connection, and controlled via a labVIEW interface. Through this interface, the power can be adjusted down to 10% of the full power. At full power, the total irradiance is 410 mW/cm 2 .

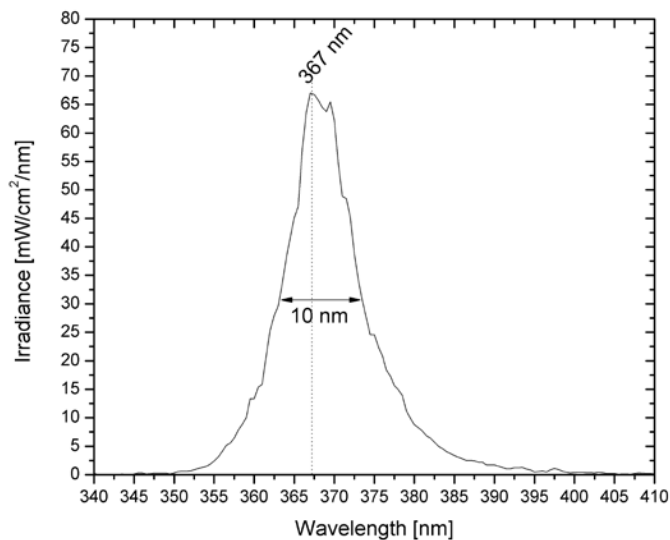


Figure S6. Irradiance spectrum of the Hamamatsu LED.

Lamp heating

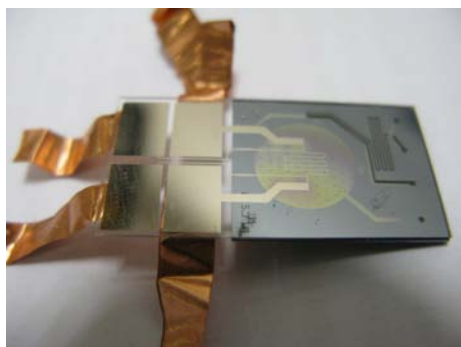


Figure S7. Schematics of the μ -reactor with a FPP resistive element inside the reaction chamber. Cu-tapes were added to the bonding pads for electrical connections.

In order to evaluate the thermal effect of the sample inside the reactor, a reactor with a FPP (Four Point Probe) resistive element inside was bonded and measured upon Hamamatsu UV-LED used for the activity measurements. The resistive element can indicate temperature change inside the reaction chamber. Figure S8 shows the temperature change in the μ -reactor when illuminated with the Hamamatsu LED at distance of 1 cm. Several conclusions can be made from the graphs. When illuminating with the Hamamatsu, the maximum in the heating from room temperature at 295.75 K is only around 4 K, which is a very minute change that will hardly affect the sample activity. The maximum of the heating is reached after only 30 seconds, after which the signal stabilizes. When the light is switched off, the response of the cooling signal is almost as fast as for the heating, indicating that the heating from the Hamamatsu is very local, and primarily involves the reactor which, due to the very small volume, cools very fast. Performing alternating 1 minute sequences where the light is on and off, as is done in order to evaluate the photocatalytic activity, the heating will reach its full effect. Further

measurements showed that an increase in the distance between the lamp and the reactor to 3 cm only had the effect of reducing the maximum temperature by 1 K. Letting gas through the reactor while illuminating at 1 cm, reduces the 4K temperature increase by 0.5 K. This is because primarily the reaction chamber is illuminated with the Hamamatsu, and only 0.01 % of the gas passes through this section due to the flow restriction of the capillary, resulting in a poor heat transport capacity. The heating response from the Hg lamp is very slow in comparison, and in the course of 45 minutes, the heating from room temperature at 295.8 K has only amounted to 3.3 K. It is clear that the maximum in temperature has not been reached at this point, but as the heating sequences during activity measurements are only of a few minutes duration, the heating from the lamp does virtually not exist. As the lamp cools off very slowly because of its large volume, running long experiments with many sequences, the heating will maybe in the worst case amount to 3-4 K.

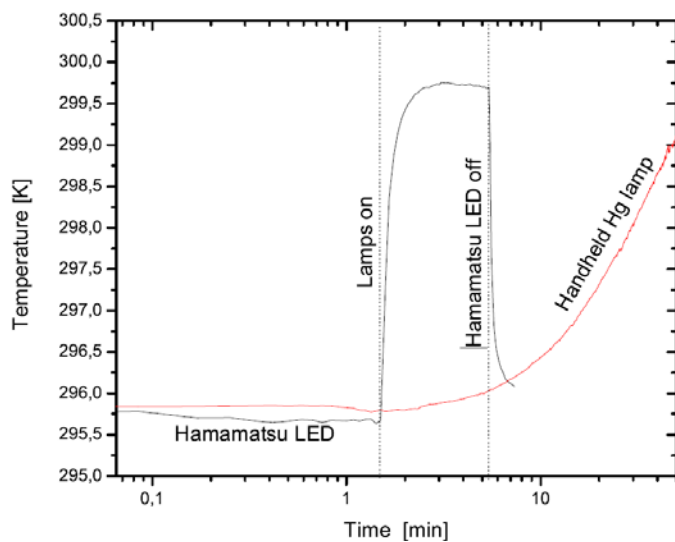


Figure S8. The temperature change inside the reaction chamber with illumination of the Hamamatsu LED and Hg lamp.