Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information for

“Suspended” Pt nanoparticles over TiO_2 nanotubes for enhanced photocatalytic H_2 evolution

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Growth of TiO_2 nanotubes

Titanium foils (0.125 mm thickness, 99.6+ % purity, Advent Research Materials) were decreased in acetone, ethanol and deionized water and then dried in N_2 stream. Anodization was conducted in a simple two-electrode electrochemical cell, in a hot H_3PO_4/HF electrolyte, at 15 V for 2 h, using a DC power supply (VLP 2403 pro, Voltcraft). The concentration of HF was 3 M and all the anodization experiments were performed by fixing the temperature of the electrolyte typically at 80 °C (these experimental conditions are similar to those reported in some of our previous works).[1-3] A Ti piece and a platinum foil were used as working and counter electrodes, respectively. After anodization, the samples were rinsed with ethanol and subsequently dried in a N_2 stream. Subsequently, the layers were annealed at 450 °C for 30 min in air using a Rapid Thermal Annealer (Jipelec Jetfirst 100 RTA), with a heating and cooling rate of 30 °C min^{-1}.

Fabrication of TiO_2 nanofibrils

The nanofibrils were formed at the opening of the tubes by soaking the TiO_2 nanotube arrays in a 4 M NaOH aqueous solution for 30 min at room temperature, in the absence of stirring. Then, the samples were taken off, washed with deionized water, and dried in a N_2 stream.

Test experiments carried out by using another alkaline electrolyte (KOH_{aq} instead of $NaOH_{aq}$) led to a similar structure of the nanofibrils (Fig. S2(a)), therefore proving that the formation of the fibrils is simply ascribed to a localized TiO_2 dissolution-precipitation reaction induced by the high concentration of hydroxide anions. We also observed that the formation of the fibrils is suppressed if the NaOH treatment is performed under stirring (Fig. S2(b)). Nevertheless, it is important to notice that the nanofibrils formation occurs without affecting the ordered structure of the nanotubes.

We also performed some NaOH treatments on TiO_2 nanotubes fabricated by conventional electrochemical anodization, *i.e.*, grown in glycerol- or ethylene glycol-based electrolytes. Noteworthy, the formation of nanofibrils did not take place when employing these nanotubes, this most likely owing to a different chemical composition of the tubes grown in organic-based electrolytes compared to ones grown in hot HF/H_3PO_4 solutions.

Pt decoration

In order to decorate the TiO_2 nanotubes, a plasma-sputtering (EM SCD500, Leica) technique was used to deposit Pt thin films. Different Pt amounts were sputtered on the samples by choosing various nominal thicknesses in the range between 0.5 – 15 nm. The amount of Pt was controlled by measuring the nominal thickness of Pt with an automated quartz crystal film-thickness monitor. This approach allowed for a fine control of Pt amount (*e.g.*, down to nominal thicknesses of 0.5 nm) and also ensured the reproducibility of deposition. The sputtering was usually carried out at 10^{-2} mbar of Ar, by applying a current of 17 mA and by using a 99.99 % pure Pt target (Hauner Metallische Werkstoffe). The average coating rate was 0.07 nm s^{-1}. After Pt decoration, the samples were annealed in Ar, at 450 °C for 30 min to induce thermal dewetting.

Characterization of the structures

For morphological characterization of the samples, a field-emission scanning electron microscope (FE-SEM, Hitachi S4800) and a high resolution transmission electron microscope (HR-TEM, Philips CM300) were employed. The crystallographic properties of the materials were analyzed by 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). X-ray photoelectron spectroscopy (XPS, PHI 5600, US) was used to characterize the chemical composition of the samples.

Photocatalytic experiments

The photocatalytic H_2 production was conducted by immersing the samples in a 20 vol% ethanol-aqueous solution and by irradiating the photocatalyst with UV light from a HeCd laser, Kimmon, Japan (λ = 325 nm; beam size = 0.785 cm^2; irradiation power = 60 mW cm^{-2}). The experiments were run in a quartz tube photocatalytic cell, sealed up with a rubber septum from which 200 μL gas samples were withdrawn and analyzed by gas chromatography (GCMS-QO2010SE, Shimadzu) to determine the amount of evolved H_2. The GC was equipped with a thermal conductivity detector (TCD), a Restek micropacked Shin Carbon ST column (2 m x 0.53 mm) and a Zebron capillary column ZB05 MS (30 m x 0.25 mm). GC measurements were carried out at a temperature of the oven of 45 °C (isothermal conditions), with the temperature of the injector set at 280 °C and that of the TCD fixed at 260 °C. The flow rate of the carrier gas, *i.e.*, argon, was 14.3 mL min^{-1}. All the experiments lasted 9 hours and the amount of evolved H_2 was measured always at the end of the experiments. For few checking runs, gas samples were withdrawn after 1, 3 and 6 h to verify that the H_2 evolution was steady over time. All the photocatalytic experiments were conducted in inert atmosphere, that is, the water-ethanol solution in the reaction tube was carefully purged with N_2 before starting the photocatalysis. This is strictly need as O_2, if present, would diminish the efficiency of H_2 production by competitively undergoing photocatalytic reduction to $O_2^{-\bullet}$ (that is, O_2 would react with conduction band electrons).

The photocatalytic experiments were carried out in ethanol-water mixtures since the presence of specific amounts of organics (*e.g.*, methanol, ethanol and glycerol) was proved to markedly trigger the H_2 production.[1,2,4-6] Precisely, ethanol acts as a hole-scavenger, meaning that the organic molecules are quickly oxidized towards several intermediates and finally to CO_2. As a consequence of the fast hole-consumption, conduction band electrons are more readily available for water reduction, thus yielding larger amount of H_2.

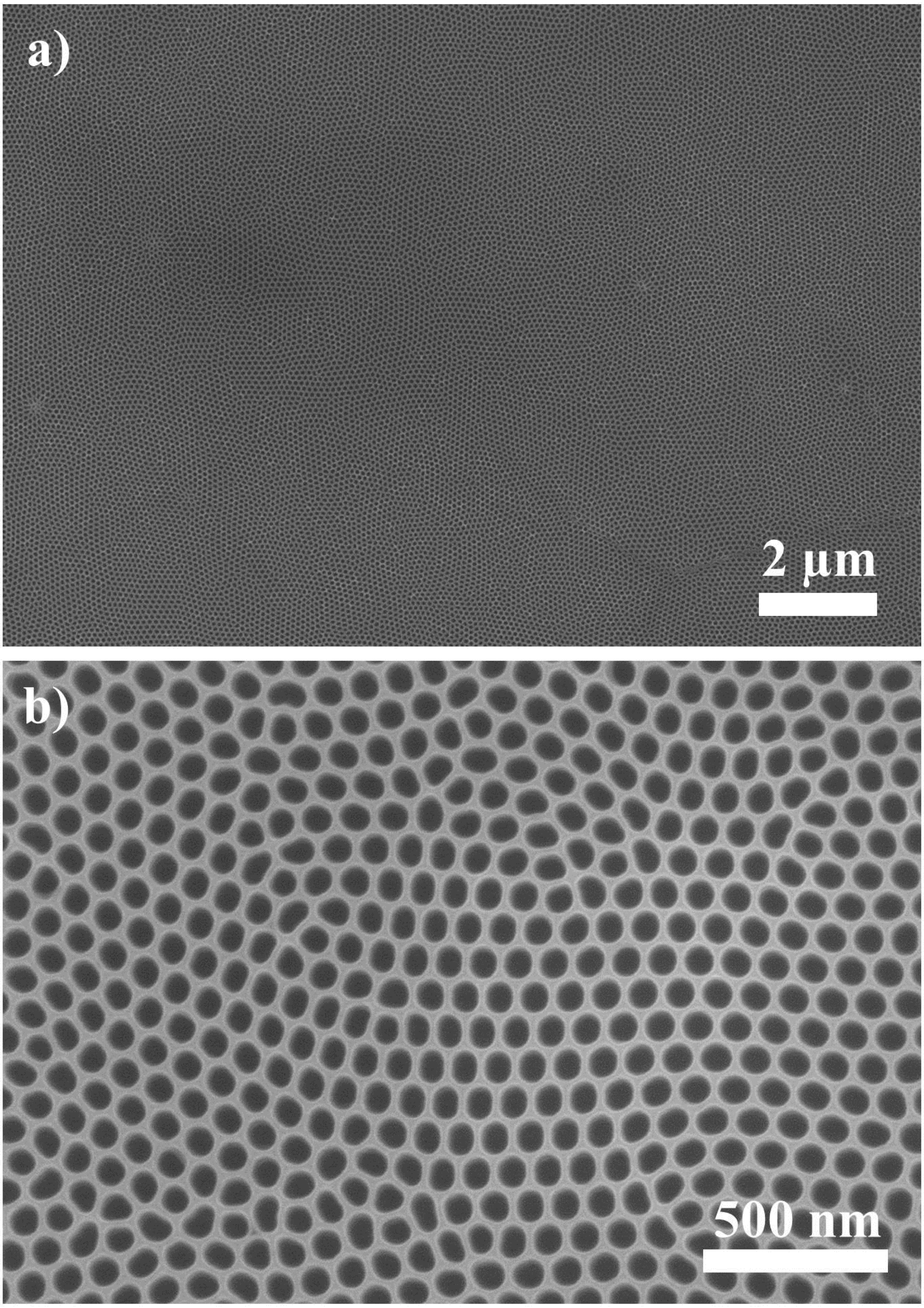
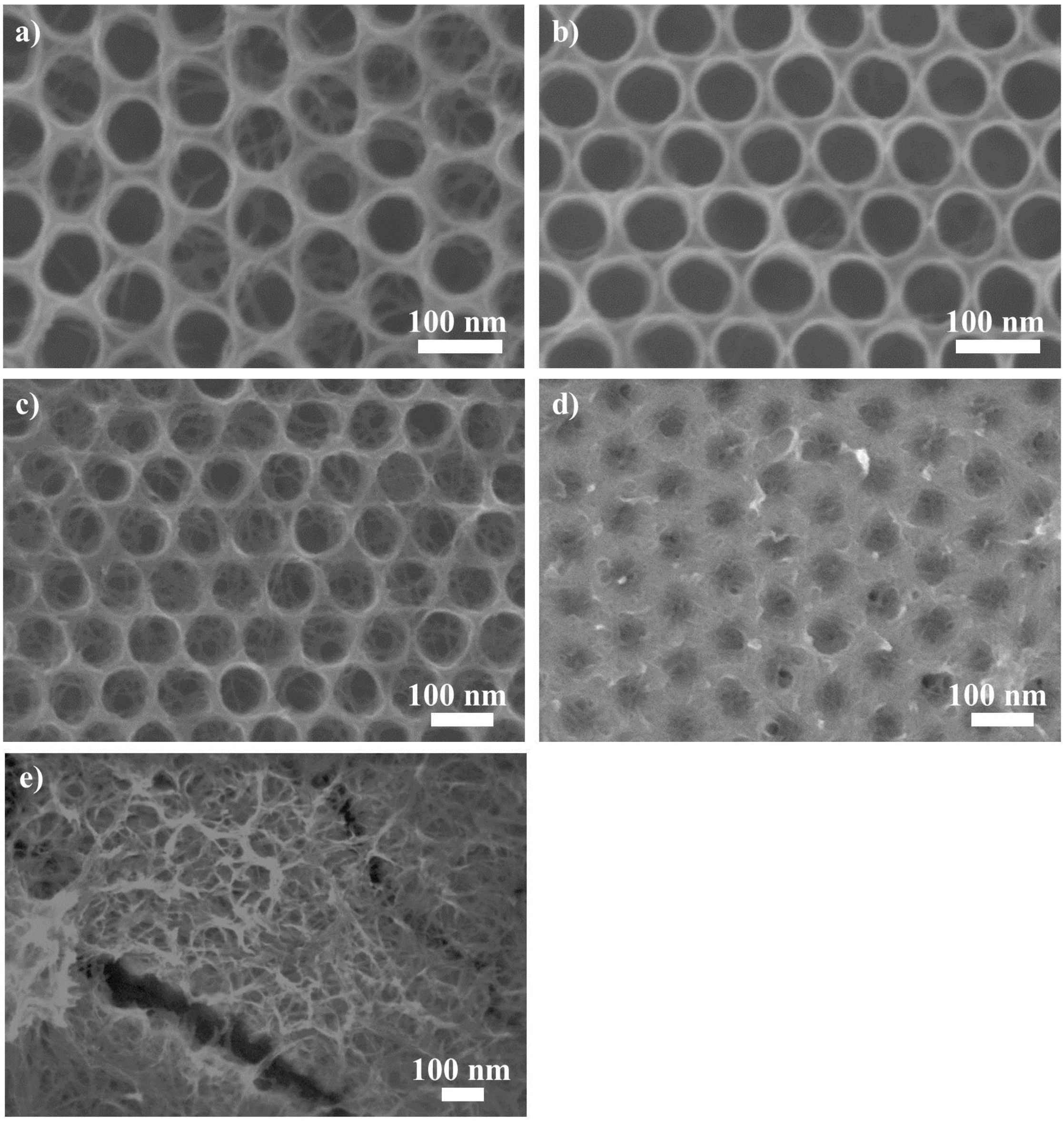


Figure S1. Top view SEM pictures of highly ordered TiO_2 nanotubes taken at magnification of a) 8 K and b) 50 K.


a)
100 nm
b)
100 nm
c)
100 nm
d)
100 nm
e)
100 nm

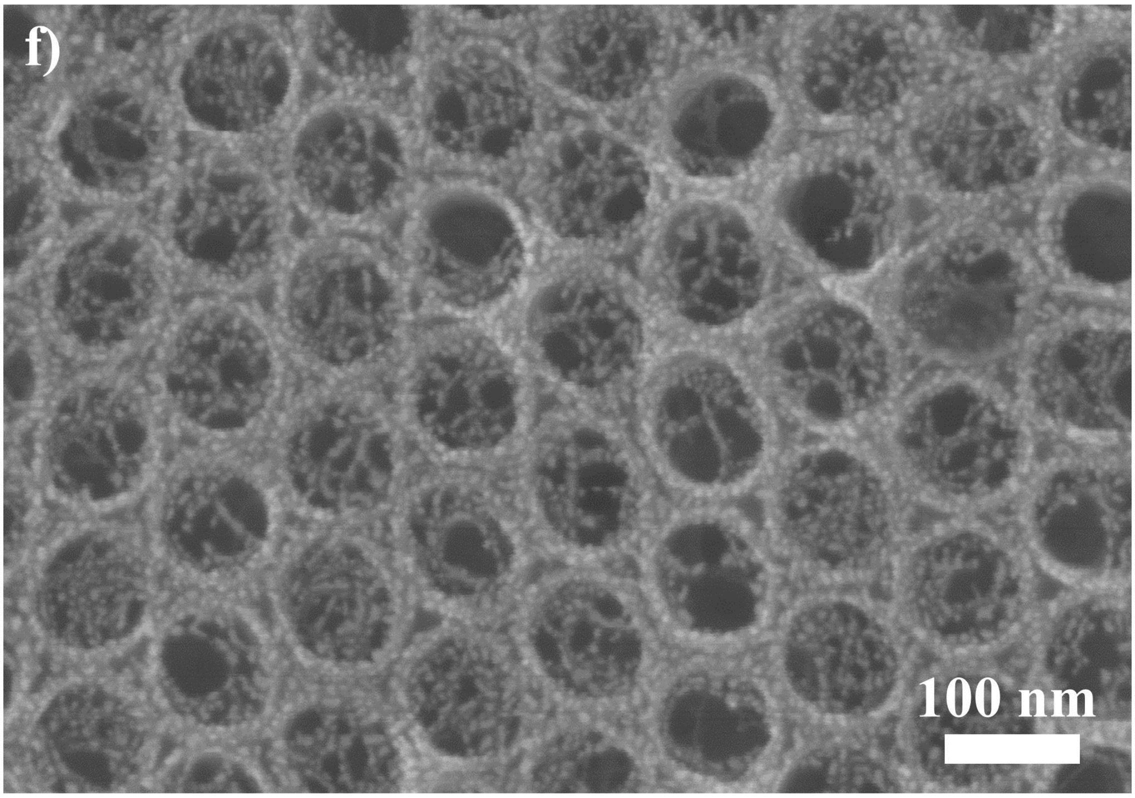


Figure S2. SEM images of nanofibrils formed: a) after 30 min-long KOH-treatment; b) after 30 min-long NaOH-treatment performed under stirring; c) after 24 h-long NaOH-treatment; nanofibrils formed by performing d) 30 min; e) 24 hours-long NaOH-treatment with amorphous nanotubes; f) suspended Pt nanoparticles formed by thermal dewetting in Ar of 1 nm-thick Pt-layer.

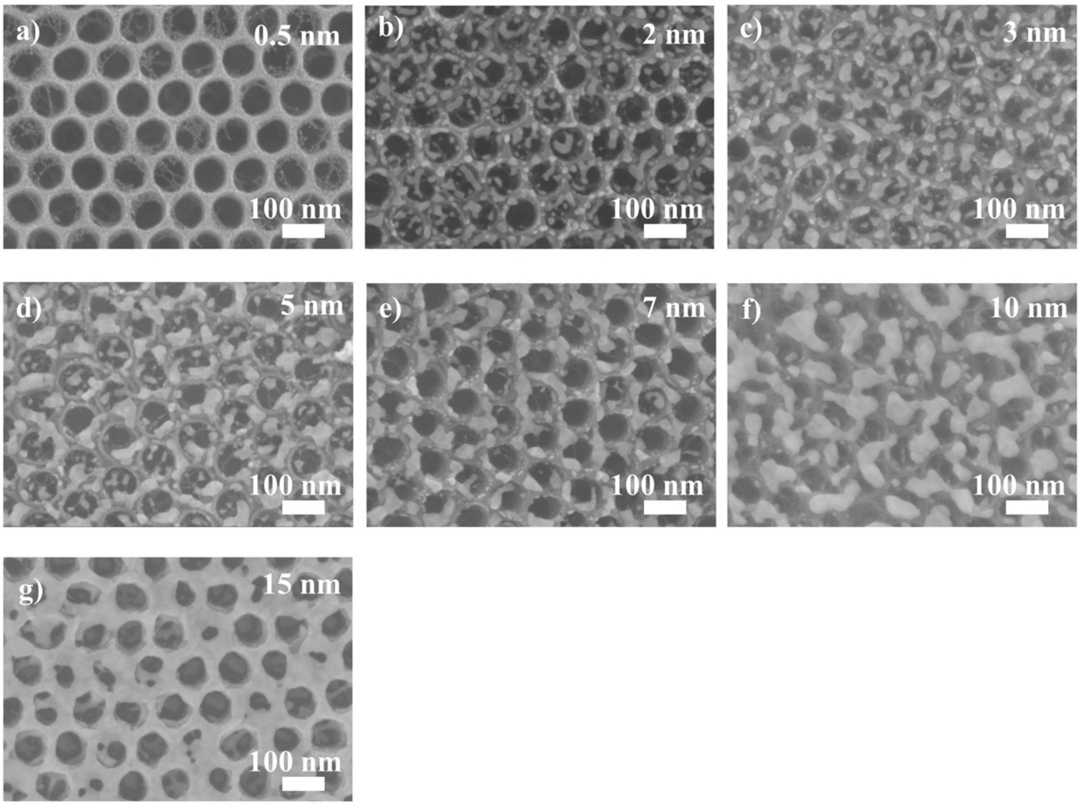


Figure S3. Top view SEM images of TiO_2 nanotubes decorated with different nominal thicknesses of the sputtered Pt film: a) 0.5 nm; b) 2 nm; c) 3 nm; d) 5 nm; e) 7 nm; f) 10 nm and g) 15 nm.

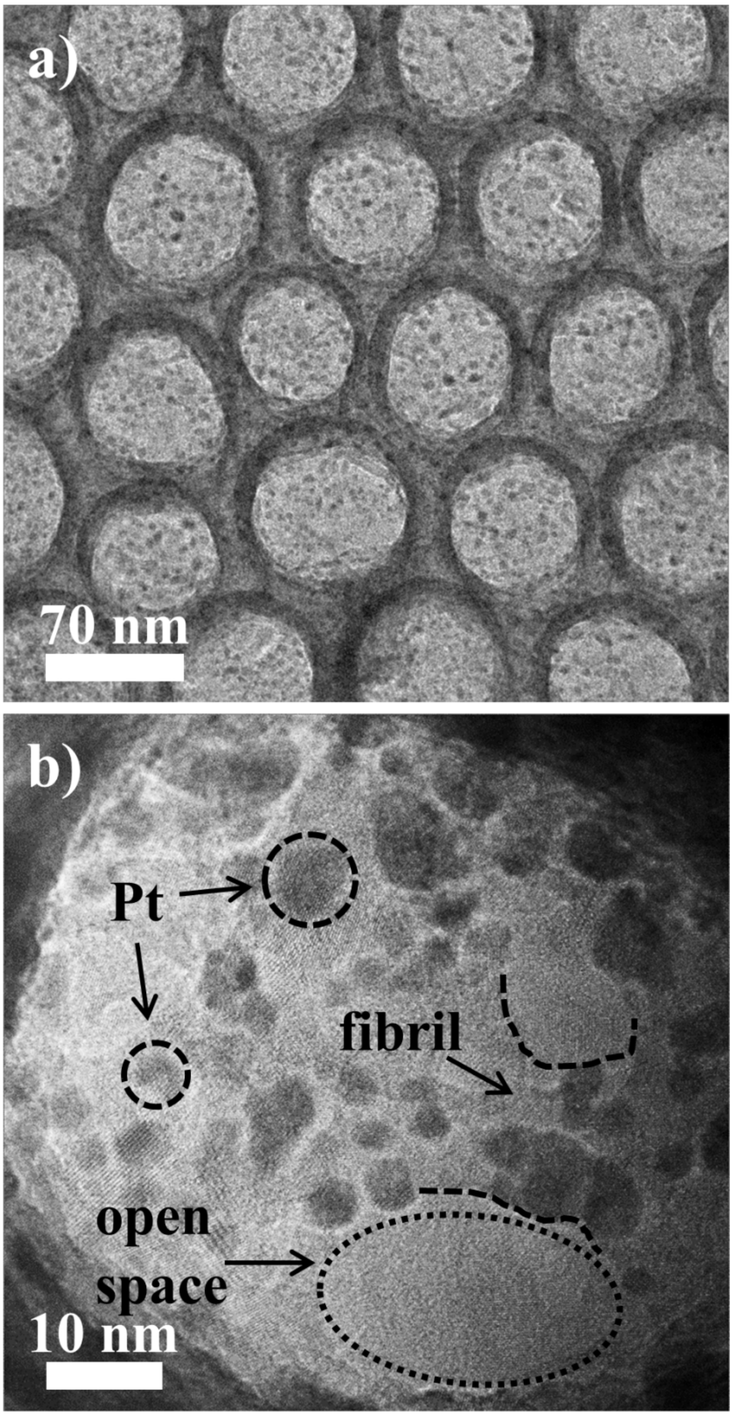


Figure S4. HR-TEM images of Pt nanoparticles suspended over TiO_2 nanotubes.

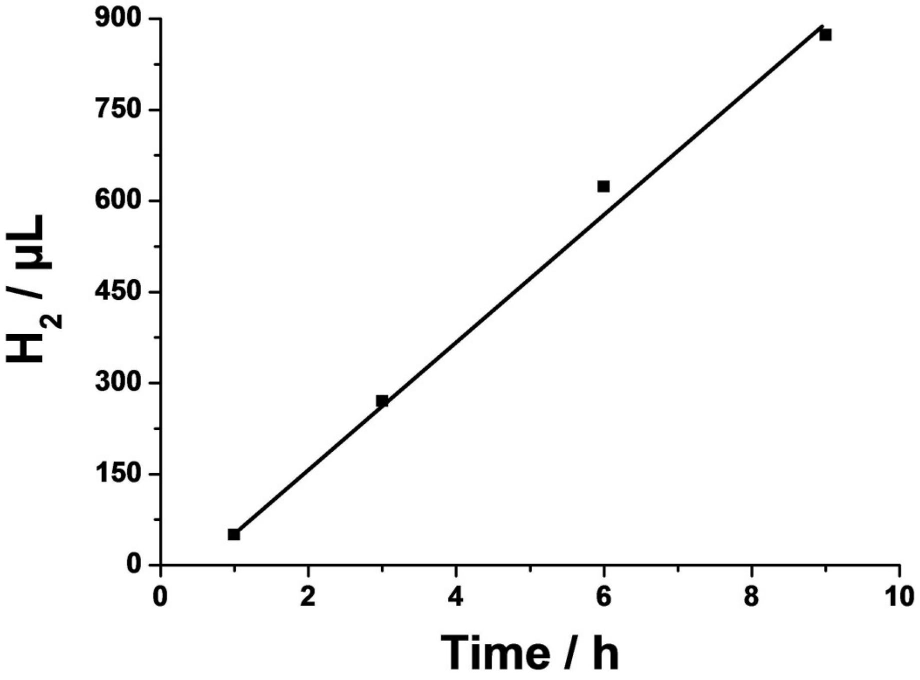


Figure S5. Amount of photo-produced H_2 measured over the irradiation time with 1 nm-thick Pt film suspended over the TiO_2 nanotubes.

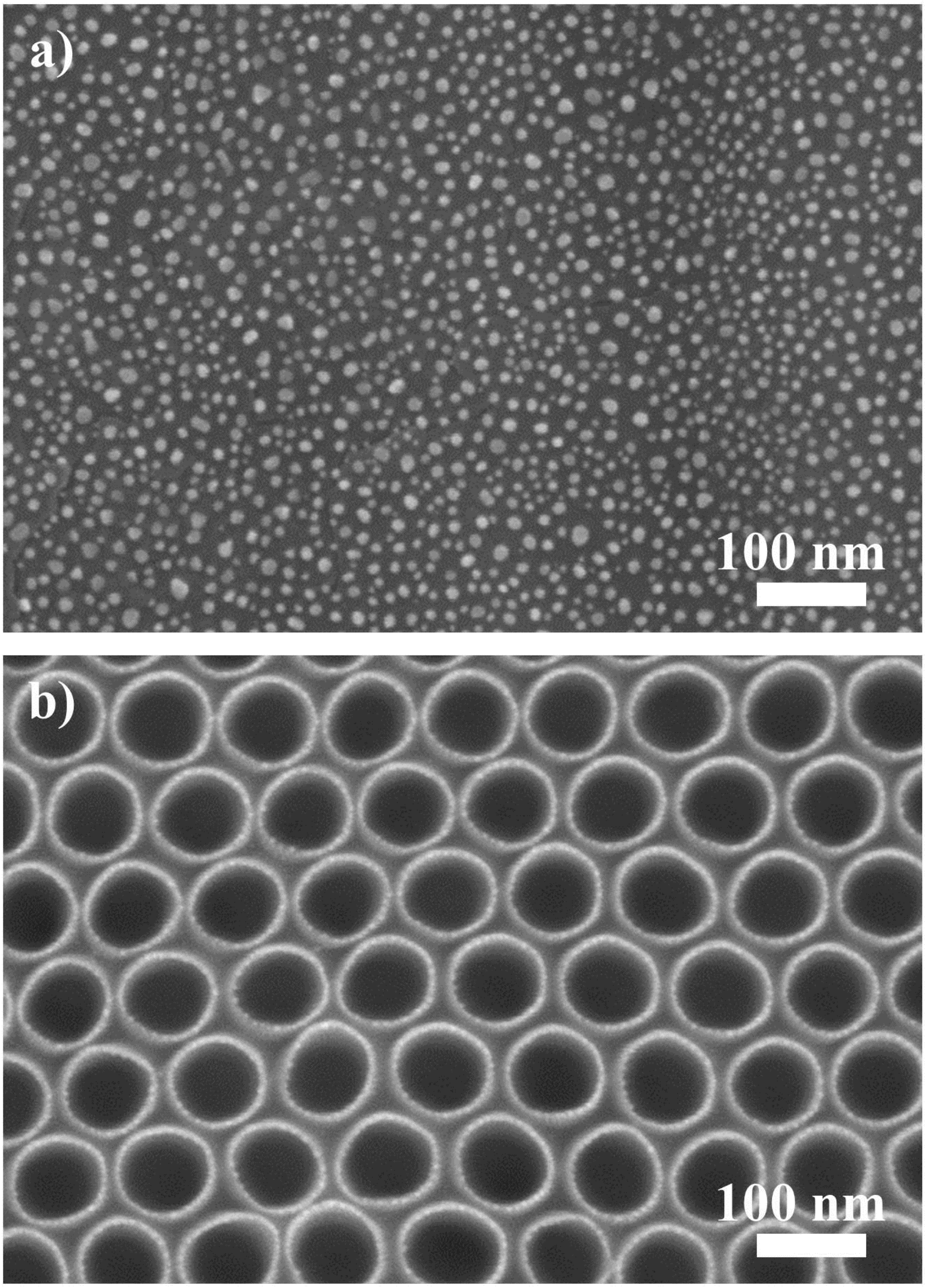


Figure S6. Top view SEM images of 1 nm-thick Pt-decorated a) TiO_2 compact oxide film (formed by a 15 min-long anodization in 1 M aqueous H_2SO_4 at 20 V) and b) TiO_2 nanotubes prepared as reported in the experimental but without growing the nanofibrils.

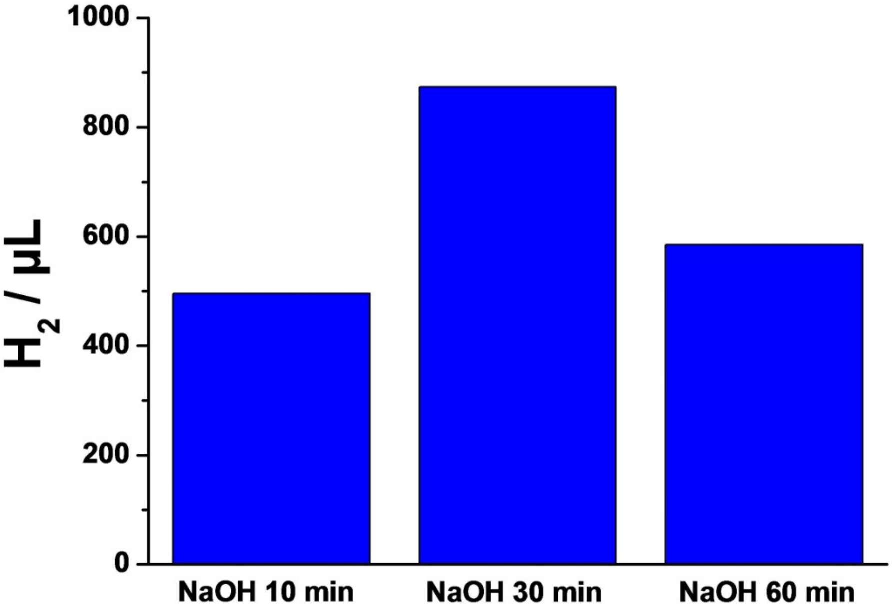


Figure S7. Photocatalytic H_2 evolution measured with 1 nm-thick Pt film suspended over TiO_2 nanotubes prepared with different durations of the NaOH-soaking treatment.

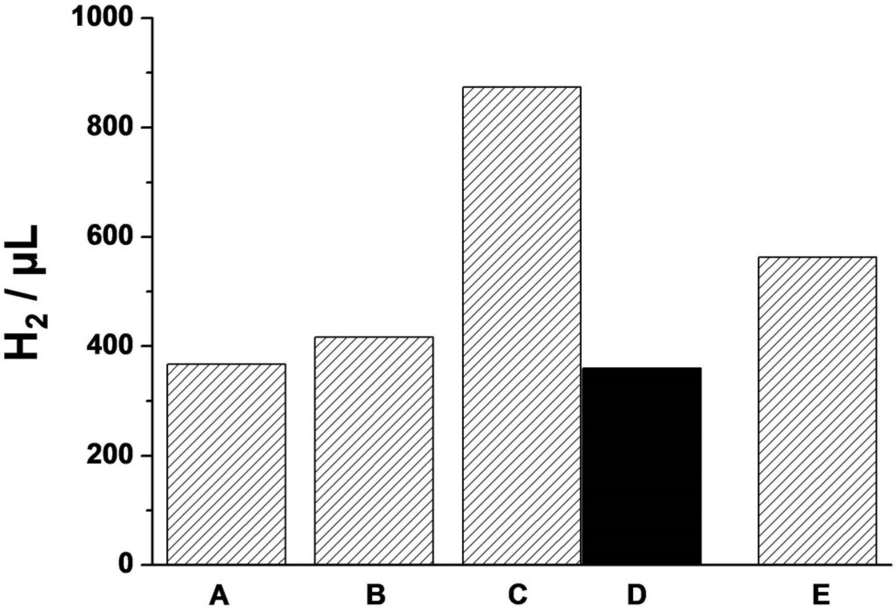


Figure S8. Photocatalytic H_2 evolution of different 1 nm-thick Pt film suspended over TiO_2 nanotubes. Samples A, B, C and E were prepared as follows: nanotube growth → air-annealing → NaOH treatment → Pt sputtering → thermal dewetting in Ar for 2, 10, 30 and 120 min, respectively. Sample D was prepared as follows: nanotube growth → air-annealing → NaOH treatment → thermal dewetting in Ar → Pt sputtering.

References

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