Establishing High Photocatalytic H₂ Evolution from Multiwalled Titanate Nanotubes

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Black TiO₂ in various forms has been investigated for numerous photochemical applications. In photocatalytic water splitting, “grey” titania forms have been reported to reach considerable H₂ generation rates without using a noble metal co-catalyst. Up to now, a variety of anatase powders or other morphologies has been investigated in grey and black forms. Here we describe that hydrothermal titanate/anatase nanotubes can show a strong noble metal free photocatalytic activity. For optimized “blackening” conditions, a drastically higher photocatalytic H₂ production can be obtained than for other nanoscale morphologies. This effect can further be improved with a very mild Pt doping that again shows a clearly stronger photocatalytic H₂ production than comparably loaded nanopowders.

The most investigated photocatalyst in the past three decades is by far TiO₂ in its various polymorphs and nanostructures. Since Fujishima and Honda initiated the aqueous photocatalysis topic,[1] more than 10,000 papers were published with respect to the photocatalytic production and storage of hydrogen (H₂). Despite this intensive research focus, the primary goal is still not met, namely an efficient H₂ production from water and sunlight. Though the principle of photocatalysis is quite straightforward, i.e. (solar) light illumination generates electron–hole pairs in the appropriately chosen semiconductor that then travel to the surface of the semiconductor and subsequently react with a neighboring red/ox species (or aqueous electrolyte), thus generating O₂ and H₂.[2–6] This reaction is in competition with direct or indirect recombination of the excited charge carriers.

TiO₂ has two main intrinsic limitations, namely as TiO₂ possess a large band gap it can only absorb UV light, and secondly, it shows a slow kinetics (i.e. the transfer of the electron from the conduction band to the environment is slow, as well as the formation of H₂). For these reasons, alternate semiconductor materials have additionally been examined; however, TiO₂ remains by far the utmost used photocatalytic research platform - this can be attributed to its stability (chemical, photochemical) as well as to environmental and cost-effective reasons. There is a wide variety of TiO₂ morphologies and their further modification, starting from anodic TiO₂ nanotubes to powders and wire arrangements, that have been employed to set off a multitude of photoinduced reactions, for more details please see refs.[2–9]. To note, in photocatalysis the most unequivocal method is utilizing TiO₂ particle suspensions, hence leading to a photocatalytic system with no external potential bias (simplifying the set up for production but requiring a separation of the gas mixture). However, for an efficient gas production under open circuit conditions a co-catalyst is commonly used, and for H₂ production this means a noble metal, M (M is Pt, Pd, or Au).[10–12] As a matter of fact, the role the M co-catalyst plays can be outlined as (1) supplying an electron acceptor and mediating electron transfer to the acceptor species present in the electrolyte solution, (2) creating metal-semiconductor solid-state junctions for trapping the electron on the co-catalyst, (3) serving as a recombination center for hydrogen, thus promoting H₂ formation (this is particularly true for Pt).[10–12] Such photocatalytic systems based on M/TiO₂ have therefore been researched as to improve their H₂ generation efficiency from water, both without or with addition of sacrificial agents (methanol, ethanol, etc.)[3,10–13].

For TiO₂ performance promoting steps were explored not only to accelerate the reaction rates but also to extend the TiO₂ light absorption from plain UV absorption to the visible range (as a result of the large band gap of TiO₂, e.g. anatase with E_g of 3.2 eV, and rutile with 3.0 eV[13]), hence enabling a proficient use of solar light illumination on TiO₂.[3,14] To overcome this limitation, band gap engineering methods have been estab-

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lished that require doping with an ample assortment of elements, such as N, S, or a full range of transition metals (for further details see refs. [21,27]). While the addition of most of these dopants in the band gap of TiO₂ facilitates visible light absorption, nevertheless, the water splitting performance does not significantly increase (i.e. still shows modest yields). This is mainly due to the fact that the introduced dopants also lead to an increased carrier recombination.

A fundamentally different approach was introduced by Chen and Mao in 2011, when they reported on ‘black’ TiO₂ [14] obtained from mesoporous TiO₂ particles subjected to high pressure and simultaneously high temperature treatment conditions in a pure H₂ environment. After Pt nanoparticle decoration, a highly increased water splitting activity was observed (without electrochemical bias). This finding was assigned to a decrease of the material’s (i.e. ‘black’ Pt-decorated TiO₂) band gap to 1.8 eV, owing to the structure of the anatase nanoparticles: an inner crystalline core surrounded by an amorphous H-containing shell [15,16]. Extensive follow-up research on ‘black’ TiO₂ accounted for substantial beneficial effects as a result of TiO₂ ‘blackening’ in a variety of applications, such as photoelectrochemical H₂ production, photocatalytic applications involving pollutant degradation and drug release, and enhanced performance of supercapacitor or battery electrodes [15-18]

Further work led to an outstanding finding in 2014 by Liu et al., demonstrating that such a high pressure/high temperature treatment of titania in H₂ can lead to photocatalytic generation of H₂ without the use of any noble metal co-catalyst. This unique characteristic was observed for a wide range of TiO₂ forms, for anodic nanotube arrays [21], powders or nanoparticles [22], mesoporous TiO₂ [23], or more complex structures (Ti/TiO₂ core-shell arrangements) [24]. Aside from the previously reported visible light absorption, hydrogenation treatments can, in addition, create in TiO₂ intrinsic cocatalytic active centers, comparable to the cocatalytic effect generated via decoration with a noble metal. Additionally, it is important to note that photocatalytic H₂ generation data in literature, comprising TiO₂ and black TiO₂, originate from titania suspensions using noble metal co-catalysts. Liu et al. and more detailed EPR work identified surface Ti⁴⁺→O₂⁻ in reduced TiO₂ to have a decisive role in the activation of the intrinsic cocatalytic active centers (i.e. without noble metal decoration) for H₂ generation [23].

Another particularly interesting form of titania are hydrothermally assembled titane tubes. These tubes can be annealed to titane/anatase, maintaining a nanotubular morphology if very mild annealing conditions are used [25]. The reason that these tubes have hardly been explored in view of “blackening” and thus activating hydrothermal titane tubes for H₂ generation without noble metal co-catalysts, is their instability during thermal treatments (thermal sintering, necking). However, herein we report that after an optimized heat and hydrogen treatment, titane/anatase mixed multiwalled hydrothermal nanotubes (HNTs) show not only a remarkably enhanced photocatalytic H₂ generation (in comparison with other TiO₂ morphologies) but also a synergistic effect between grey TiO₂ and Pt can be found. Further examination of the high temperature hydrogenation of titane nanotubes (HNTs) morphology, crystallinity and chemical structure, i.e. by TEM, XRD and XPS, combined with BET measurements and particularly EPR, describe the effect of different degrees of surface hydrogenation, leading to different structural defects. The intrinsic activity of the hydrogenated titanate samples for photocatalytic H₂ evolution reaches a maximum after a treatment in H₂ at 500 °C. Under these conditions, a partial reduction of the Ti⁴⁺ in the tubes has taken place to Ti⁴⁺→O₂⁻. The connection between surface Ti⁴⁺→O₂⁻ species and photocatalytic activity is very straightforwardly apparent from a comparison of EPR and photocatalytic H₂ generation measurements. Remarkably, the hydrothermal nanotube morphology provides a strongly enhanced activity (even without co-catalyst) compared with other titania nanomorphologies. We also show that decoration of the grey nanotubes with Pt further augments the photocatalytic H₂ evolution activity and again with a stronger enhancement than for other studied morphologies.

In essence, titane tubes are produced from a titania source that, when treated in an autoclave under strongly alkaline conditions, leads to the formation of multi- or single wall tubes with tube walls in single atomic dimensions (with distinct titanate units). In our case, we used commercial TiO₂ powder dispersed in NaOH solution that underwent a hydrothermal treatment for 48 h at 130 °C followed by neutralization, washing and annealing (see experimental section for more details and also literature [26]). After synthesis, the plain tube powder is white (Figure 1a), whereas after H₂ annealing, with increasing H₂-temperature, the tubes become darker. Clearly, a grey-blue to black appearance occurs (this general trend is in line with frequently reported formation of color centers for hydrogenated or otherwise reduced anatase powder). For Pt-dosed samples (see Supporting Information Figure S1b), the color shifts from slightly grey (as formed) to blue after the heat treatment. It is noteworthy that generally the structural decay temperature is also around 500 °C. However, the SEM images in Figure 1f-i show that in our case after synthesis typical nanotube shapes are obtained that remain unchanged by the H₂ annealing at 500 °C (Figure 1b–e).

TEM images in Figure 1b–e correspond to samples before and after hydrogenation (d–e), as well as to Pt-dosed samples (c,e). The images show clearly the single unit rolled titane walls. Lattice fringes with interplanar distances of 0.36 nm and 0.73 nm can be identified in a single nanotube (Figure S2i), which correspond to crystallographic planes of anatase (101) and Na₅₋₃Ti₄O₁₀ (110), respectively. As mentioned, the challenge of these tubes is to maintain their morphology during annealing. For pure acidic titanes we could hardly maintain the morphology (due to sintering). In air the tubes were stable only up to 300 °C [21,27] and up to 350 °C in H₂ containing environment. In contrast, partially sodiated tubes were ascertainmented as stable at temperatures of up to 400 °C in air and up to 500 °C in H₂. The corresponding SAED patterns show in every case the presence of anatase and to a lower extent sodium titane (Figure S2j). Pt signals could be detected in samples nominally containing 0.2 at-%.
Both sets of nanotubes, Pt-free and Pt-containing, were tested after H₂-annealing for their H₂ generation performance. Figure 2 shows results HNTs (Figure 2a) and Pt–HNTs (Figure 2b) after hydrogenation at different temperatures. Clearly, both HNT and Pt–HNT show a strong increase in their photocatalytic H₂ evolution rate for increasing annealing temperatures up to 500 °C, whereas for higher temperatures the activity drops again. The inset shows corresponding data taken from literature obtained for a similar Pt loading on anodic TiO₂ NT arrays and for anatase nanopowder (Sigma). Also for these morphologies a maximum activity for the non-platinized as well as the platinized samples was obtained at 500 °C. For all samples of powder and NTs, a grey color at 500 °C and a black color at 700 °C was observed. Figure 2c,d shows light absorption measurements for HNTs and Pt-HNTs. From the spectra, for all samples a primary band-gap around 3.3–3.5 eV can be identified; please note that already the as-formed nanotubes contribute to the H₂ production reaction. (In previous work, this has been ascribed to trapped carriers of low mobility that finally just recombine rather than being promoted to the conduction band.) In line with these findings, also in our experiments with a 450 nm laser no significant amount of H₂ evolution could be observed.

Figure 3a–b show the X-ray diffraction (XRD) patterns of the TiO₂ and HNT samples studied in Figure 2a,b. In all samples, the presence of anatase (TiO₂) and sodium titanate (NaₓTiO₂) can be identified; please note that already the as-formed nanotubes consist of a mixture of anatase and sodium titanate. If the full width at half maximum (FWHM) is assessed (applying the Scherrer approach)39 a decrease of the FWHM of the anatase peak at ≈24.5° with increasing hydrogenation temperature up to 500 °C is observed, e.g. for as formed TiO₂ a FWHM of 0.855 °C is obtained and for TiO₂ hydrogenated at 500 °C of 0.645 indicating a better crystallinity. With further increasing the temperature, additional peaks appear in the XRD patterns for hydrogenation temperatures of 600 and 700 °C; these can be ascribed to the formation of Magneli phases.30 Interestingly and in contrast, the Pt treated samples maintain the plain titinate/anatase signature even at higher temperatures of 700 °C, indicating that, in line with literature32 small amounts of Pt stabilize the anatase phase.

SEM images after treatment (see Figure S2) show a significant change in morphology for tubes and particles annealed at 600 °C and 700 °C. The tubes deteriorate by annealing at these temperatures. For particles treated at higher temperatures, an extremely thin layer is barely noticeable on the outside of particles in HR-TEM. Nevertheless, this amorphous layer is not enough to alter the diffraction patterns measured in XRD. Please note that such amorphous shells at the fringe of the particles were already described for black titania after various
In addition, more interesting is the Pt peak, as exemplified in Figure 3c for the as formed Pt-dosed sample (Pt–TiO$_2$), that shows the presence of metallic Pt (Pt$^+$) with the Pt$^{4f}_{7/2}$ at $\approx$ 69.8 eV (spin separation of 3.35 eV) and Pt oxides in the form of Pt$^{2+}$ and Pt$^{4+}$ (spin separation of 3.35 eV, Pt$^{4f}_{7/2}$ with Pt$^{2+}$ at $\approx$ 71.2 eV and Pt$^{4+}$ at 73.2), with 52.2% Pt$^+$, 15.6% Pt$^{2+}$ and 32.2% Pt$^{4+}$. For the hydrogenation treatment at 500 °C, for the Pt-dosed sample (see the fitted peak for Pt-HNT in Figure S4d), the metallic Pt increases to 64.1% and the oxides decrease to 9.3% and 26.6% respectively.

The presence of Ti$^{4+}$–O$_x$ defects on a titania surface are vital for the generation of H$_2$ gas using titania dioxide catalysts. We were able to quantify these Ti$^{4+}$–O$_x$ defects using EPR spectroscopy carried out at 95 K for selected reduced samples (500 or 700 °C), see Figure 4 – details are given in the experimental section and Figure S5–S8. The as formed TiO$_2$ sample shows only a minor paramagnetic response that is attributed to the usual lattice defects observed in commercially available anatase particles. The reduced titanate samples show extreme differences in peak signature and intensities, which can be simulated due to three isotropic species with g$_{iso}$ = 1.93 (s1), g$_{iso}$ = 1.97 (s2), g$_{iso}$ = 2.01 (s3). The sharp EPR signal centered at g$_{iso}$ = 2.01 can be assigned to naturally occurring Ti$^{4+}$–O$_x$ defects in regular lattice positions, which are commonly present in anatase samples. The exposed Ti$^{4+}$ on the surface – either amorphous or distorted lattice – was detected at a g-value of g$_{iso}$ = 1.93. (22,31–39) For the reducing treatment at a higher temperature (700 °C), the ratio between s1 and s2 changed considerably with the signal of s1 decreasing and the

Figure 3. X-ray diffraction patterns after different hydrogenation treatments of a) TiO$_2$ b) Pt–TiO$_2$ nanotubes; c) XPS peak of Pt4f of Pt-titanate and fitting; d) Na1s, e) O1s, f) Ti2p, and g) C1s for Pt-titanate; atomic percent of titanate in 'black' TiO$_2$ attributed to these layers in enabling visible light photocatalysis.

Figure 4. EPR measurements for titanate samples hydrogenated at 500 °C and 700 °C a) Pt-free and b) dosed Pt; c) BET measurement.
signals of s2 and s3 increasing. This indicates that reducing at higher temperature (700 °C) leads to formation of significantly more defects, possibly due to a partial conversion of anatase to Magnéli phases. The existence of a different type of defect structure at giso = 1.97 is discernible due to the differences in the major components of the paramagnetic signature.

As we have previously demonstrated, the ‘grey’ sample with the highest activity displays a paramagnetic center with a g-value of giso = 1.93 (but in a much lower concentration as compared to the ‘black’ material). In the measurements for Pt-decorated samples (Figure 4b) the same three species could be detected as in the Pt-free sample, but with less difference in the ratio between s1 and s2. For the reducing treatment at a higher temperature (700 °C) the intensity of the signal s3 is increased, as was anticipated. The presence of Pt itself, although strongly enhancing the photocatalytic performance, does not cause a strong change in the defect signature of the titanate tubes. However, XPS confirmed a partial reduction of the Pt oxides to metallic Pt for hydrogenation at 500 °C.

The Pt-grey anatase as compared to the Pt-white anatase provides i) additional H2 formation centers (Ti4+/3-); ii) the possibility of an energy (electron transfer) cascade TiO2 → Ti3+ + Pt; iii) the Pt to be present in a more metallic state. All these effects may contribute to the observed synergy in the catalysis of the photocatalytic H2 generation on grey Pt–TiO2.

In summary, in this work, we fabricate mixed titanate/anatase hydrothermal nanotubes (with and without mild Pt dosing) and expose them to different thermal hydrogenation treatments and thus form ‘grey to black’ tubes. We then compare the performance of the hydrothermally darkened titanate/anatase nanotubes (Pt dosed and Pt free) for photocatalytic H2 generation with most common TiO2 morphologies. We find that even the Pt-free grey hydrothermal nanotubes provide up to 10 times higher photocatalytic efficiency than standard “blackened” nanopowder or “blackened” anodic TiO2 nanotubes. Mild Pt dosing further improves, as expected, the efficiency. The optimized hydrogenation treatment leads to a presence of an optimized amount of surface Ti4+/3- defects that act as co-catalytic centers for the photocatalytic H2 evolution. For Pt loaded tubes an enhancement of the Pt co-catalytic efficiency induced by hydrogenation can be ascribed to a further reduction (to the metallic state). We ascribe the highest beneficial effect of the mixed bi-crystalline titanate/anatase composition in the hydrothermal tubes, in comparison to classic TiO2 material, to the formation of an electronic junction that aids charge separation and in turn allows an easier collection of the charges at the catalytic sites.

**Experimental section**

**Synthesis of TiO2 nanotubes** TiO2 nanotubes samples were synthesized by the alkaline hydrothermal method demonstrated by Kasuga et al.[26] In a typical synthesis, 6 g of commercial TiO2 powder (P25, Degussa AG, Germany) was dispersed slowly in 120 mL of 10 M NaOH solution under constant stirring. This suspension was stirred for 30 min, and moved into a Teflon-lined stainless steel autoclave, sealed, and placed in an electric oven and temperature at 130 °C for 48 h. The resulting material after the hydrothermal treatment was collected and filtered, neutralized with 0.1 M HCl solution and washed with deionized water for five times. Then, it was dried in air at 100 °C for 12 h and finally calcined in air at 400 °C for 5 h.

**Synthesis of Pt/TiO2 nanotubes** Pt nanoparticles were synthesized by a simple chemical reduction method in which NaBH4 was used as a reducing agent, polyvinyl alcohol (PVA) as a capping agent, and H2PtCl6 as the Pt source. In a typical synthesis, PVA (20 mg) was dissolved in hot deionized water (10 mL), and 5 mL of this PVA solution was then combined with 5 mL of H2PtCl6 aqueous solution (0.01 M) under stirring. Then, 5% NaBH4 solution was added drop by drop to the mixture. The color of this solution incrementally changed to a dark brown (from light yellow). Finally, the calculated amount of TiO2 nanoparticle powder was added under stirring to the solution which contained Pt nanoparticles, while maintaining the stirring for 30 minutes longer. The obtained product was five times washed with distilled water and then dried at 100 °C for 4 h.

**Hydrogenation TiO2 and Pt/TiO2** nanotube powders were annealed in pure H2 (Linde, 99.99%) flow in a flow furnace (Heraeus, ZEW 1450-4, Germany) for 1 h, at atmospheric pressure and at temperatures in the 300–700 °C range.

**Characterization** The nanotube powders were evaluated by using a scanning electron microscope (SEM, Hitachi, S-4800) to confirm their morphology and structure and their composition was studied by an energy-dispersive X-ray analyzer (EDAX Genesis) equipped to the SEM chamber. Please note that the powder samples were fixed with silver glue on a holder. The morphology of the nanotubes was in addition evaluated by transmission electron microscopy (TEM) on a Philips CM30 TEM. X-ray diffraction (XRD) patterns were measured on an X’pert Philips MD (equipped with a Panalytical X’celerator detector) with a graphite monochromatic CuKα radiation (λ = 1.54056 Å). The XRD diffractionograms were subjected to a Rietveld Analysis using a MAUD software by Luca Lutterotti.[24,25] The chemical oxidation states were evaluated by X-ray photoelectron spectroscopy (XPS, PHI 5600) and calibration of the spectra was performed to the C1s peak (284.8 eV). Peak fitting was performed in Multipak software, considering the large asymmetry of the metallic Pt peak and using a Gaussian and Lorentzian mixing line shape with a Shirley background treatment and considering the background of the bare sample. The surface area of the nanotube layers

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was determined by nitrogen sorption experiments, by means of a volumetric gas sorption analyser (Nova4200e; Quantachrome) at 77 K (liquid nitrogen temperature). Before measuring, the samples were degassed under vacuum for 2 h at 120 °C. The mass-specific surface BET area$^{20,41}$ was resolved by a 5-point determination in the 0.05 < p/p$_0$ < 0.3 relative pressure range.

To follow the presence of the defects in the reduced samples, Electron Paramagnetic Response (EPR) spectra were acquired on a JEOL continuous wave spectrometer JES-FA200 (outfitted with an X-band Gunn diode oscillator bridge, a cylindrical mode cavity and a N$_2$ cryostat). A similar amount of the nanotube samples was used for measurements (≈20 mg) and measurements were performed in the solid state under argon atmosphere in quartz glass EPR tubes at 95 K. The acquired spectra were measured under the following conditions: temperature 95 K, microwave frequency n = 8.959 GHz, modulation width 1.0 mT, microwave power 1.0 mW, modulation frequency 100 kHz, a time constant of 0.1 s. The data was further analyzed and simulated in the “eview” and “esim” softwares written by E. Bill (MPI for Chemical Energy Conversion, Mülheim an der Ruhr).

To measure the open-circuit photocatalytic H$_2$ evolution, 2 mg of the nanotube powder was mixed with 10 mL aqueous methanol (50 vol.%) solution. The quartz reactor was purged with Ar for 30 min as to remove the oxygen from the solution mixture, and following the reactor was sealed. To uniformly disperse the powder, 450 nm laser were used as light sources and the investigated suspensions were illuminated for 2 h and for 24 h when evaluating the stability.

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Conflict of Interest

The authors declare no conflict of interest.

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