Self-enhancing H₂ evolution from TiO₂ nanostructures under illumination

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Abstract: In the present work, we show how illumination of anatase in an aqueous methanolic solution forms Ti^{3+} sites that are catalytically active for the generation of dihydrogen (H_2). With an increasing illumination time, a light-induced self-amplification of the photocatalytic H_2 production rate can be observed. The effect is characterized by electron paramagnetic resonance (EPR) spectroscopy, reflectivity, and photoelectrochemical techniques. Combined measurements of H_2 generation rates and *in-situ* EPR spectroscopic observation over the illumination time with AM 1.5 or UV light establish that the activation is accompanied with the formation of Ti^{3+} states, which is validated through their characteristic EPR resonance at $g=1.93$. We show that this self-activation and amplification behavior can be observed for anatase nanoparticles and nanotubes.

Keywords: H_2 generation • Nanotubes • Photocatalysis • Self-activation • Ti^{3+} defective states

TiO₂ belongs to the most widely studied oxide semiconductors for photocatalytic production of H₂ from aqueous solutions.^[1–4] In TiO₂, not only is the conduction band situated at an energetic position that allows a transfer of photogenerated electrons to aqueous media – and thus the reaction of H⁺ to H₂ – but also it provides an almost unique high resistance against chemical and photocorrosion.^[2–7]

However, the photocatalytic H₂ production from aqueous electrolytes shows a very slow kinetics on TiO₂ surfaces.^[2,3,7] Therefore, in virtually all photocatalytic studies, for example using nanoparticle-suspensions, decoration of titania with co-catalysts is used to accelerate the H₂ evolution kinetics. Most effective but costly co-catalysts are noble metals, such as Pt, Pd, or Au.^[8,9] These co-catalysts mediate the transfer of the photogenerated charge carriers to the electrolyte.^[2,3,7,10]

Recent reports have, however, demonstrated a fully noble-metal-free approach for photocatalytic hydrogen generation from water; namely by using specific reduction treatments of anatase titania. Hydrogen annealing of titania was shown (for anatase nanotubes and powders) to lead to so-called “grey” titania, this material being intrinsically active for photocatalytic H₂ evolution.^[11–13] Specific for this material is that Ti³⁺ states are formed that are in an off-lattice position – that is with a characteristic EPR signature resonance at $g \approx 1.93$.^[14] This form of reduced titania (“grey” titania) shows, without any extrinsic (noble metal) co-catalyst, substantial photocatalytic H₂ generation. This grey titania should be distinguished from the widely studied “black” titania (introduced by Chen and Mao^[15]) that can be produced under stronger reducing conditions. For this black titania significant photocatalytic H₂ activity is not achieved without a noble-metal-co-catalyst (typically a Pt decoration of ≈ 1.0 wt%).^[15–17] In grey titania, instead of the noble metals, the specific shallow Ti³⁺ defect states in grey TiO₂ mediate photoelectron transfer to H₂O/H⁺ and thus promote the generation of photocatalytic H₂.^[11–14] The crucial role of the nature of the defect states for

photoelectrochemical properties and photocatalysts has widely been described in literature.^[11,14,18,19]

A well-elucidated approach to form reduced titania is the photoinduced reduction of TiO_2 .^[2,20,21] In essence, if TiO_2 is illuminated in organic solvents (that serve as hole capture agents), and in the absence of air (dioxygen), a coloration of the material can be observed (the color of titania typically turns from white to blue or black).^[2,20] This color change has been ascribed to the formation of sub-oxides in titania (namely $\text{Ti}^{3+}\text{-O}_\text{v}$ species) that form various electronic states in the band gap of TiO_2 .^[2,22,23]

In this work, we test the feasibility to use this photoinduced reduction to create, *in-situ*, energetically suitable Ti^{3+} states that can act as an intrinsic co-catalyst for photocatalytic H_2 evolution. This would allow to build-up light-induced, self-amplifying, photocatalytic active titania in a one-pot approach. With this goal we carried out investigations on anatase nanoparticles (NPs) that are commercially available as well as on anodic nanotube layers (NTs). The nanotube layers provide directly back contacted electrodes for defined electrochemical investigations. The TiO_2 NT-layers were grown as described in the experimental section to a length of 7 μm , and then were annealed to anatase by a heat treatment in air at 450 °C for 1 h. The photocatalytic H_2 production rates were evaluated by dispersing/immersing powder and NT samples (respectively) in a H_2O /methanol solution under AM 1.5 (100 mW/cm^2) illumination, or alternatively by using a UV light source for illumination (LED, 365 nm, 90 mW/cm^2). The H_2 evolution amount was quantified in regular intervals by gas chromatography (for details, please see the experimental section).

Figure 1 shows an overview of the photocatalytic H_2 evolution performance from anatase powders (**Figure 1a**) and nanotubes (**Figure 1b**) over the illumination time. Clearly, longer illumination times can activate the samples for photocatalytic H_2 evolution, this for both powders and NTs. The results of **Figure 1** also illustrate that AM 1.5 as well as plain UV

illumination can induce activation of titania for noble-metal-free photocatalytic H₂ evolution. In every case, a very low H₂ production is observed in the first phase. For example, for powders under 365 nm illumination, almost no H₂ evolution could be detected for the first 3 hours, however, over time the rate shows a steady increase that can reach up to 8.1 $\mu\text{l/h}$ (corresponding to 172 $\mu\text{mol h}^{-1} \text{g}^{-1}$) after 24 h of illumination.

Cycling experiments (**Figure 1c**) show that the H₂ evolution rate shows this characteristic exponential growth (initiation of active centers) only in the first cycle (first 24 h), in the following cycles a steady, nearly linear increase of the H₂ production is observed. Notably, the H₂ production becomes enhanced with each illumination day (10.3 and 12.5 $\mu\text{l/h}$ for the second and third cycle respectively). This indicates that the increased H₂ generation occurs by light-induced activation of the catalyst by Ti³⁺-Ov surface defects which particularly dominates the beginning of the process. The defects are accumulated and (despite of interruptions of the illumination and nitrogen purging before beginning a new cycle) remain active sites in the following cycles of photocatalytic H₂ generation.

H₂ evolution was also studied under 10%, 50%, 200% intensity of the LED, 365 nm, 90 mW/cm² intensity, leading to 2.4, 7.1 and 12.9 $\mu\text{l/h}$ H₂ production after 24h. Results of these measurements (**Figure 1d**) confirm that even with low light intensity (10%) and long illumination, increasing hydrogen will be generated due to the light-amplification effect. The produced H₂ volume over time for all light intensities follows an exponential relationship, however for high light intensities (200%) the relationship is already close to linear (likely due to a very quick saturation of defects/active site formation).

As expected, during illumination, a change of color of the samples can be observed, as shown for nanopowders in **Figure 1e**. The color change can be quantified by reflection spectra taken for powder samples (**Figure 1f**) which show an increase in absorption over the entire visible range. As well established in literature, if titania is illuminated in the absence of oxygen, the

lack of an electron scavenger leads to self-reduction and formation of $\text{Ti}^{3+}/\text{O}_v$ states.^[2,18,24] It should be noted that plain visible light illumination could not initiate darkening nor H_2 evolution. Moreover, darkened powder, exposed to visible light, could not generate any H_2 (neither for powder nor for nanotubes). This clearly shows that the enhanced intrinsic photocatalytic H_2 generation activity in these darkened powders is not connected to an enhanced visible light absorption of the reduced material.

Figure 2 and **S1** show features of the titania samples used in this study before and after illumination. The SEM images in **Figure 2a** and **S1a** illustrate that anatase powder before and after illumination keep their morphology with an average particle size of 25 nm. Also, in SEM images, no morphological changes of the nanotubes are observed after illumination (**Figure 2b** and **Figure S1b**). In addition, the anatase powder particles before and after 24h UV illumination were studied by high-resolution TEM (HR-TEM) – typical TEM images are given in **Figure S2a** and **S2b**. For all specimens, HR-TEM shows a typical anatase lattice spacing of 0.35 nm in the particle core. In spite of an analysis of many particles, it cannot be unambiguously determined whether there is any difference in the TiO_2 anatase powders caused by illumination. This is due to the fact that commercial anatase nanopowders provide damaged particle fringes; i.e. no light induced amorphization of the particle outer shell could be determined. This is in line with XRD patterns of titania powders and TiO_2 NTs that show identical anatase peaks before and after illumination (**Figure 2c,d**) at 25.3° , 48° , 53.9° and 55.1° (PDF card No. 01-071-1166). The peaks at 38.4° , 40.2° , 53° and 70.2° are ascribed to titanium metal peaks originating from titanium substrate from TiO_2 nanotubes. No clear change on the peak intensity and full-width at half maximum (FWHM) is observed after UV illumination, which additionally indicates that there is no change in anatase crystallinity due to illumination. Furthermore, from XPS characterization of the titania powder, no significant changes are apparent (**Figure 2e,f**). For example, the O1s, and Ti2p peaks before and after

illumination do not show significant variations in shape or elemental ratio (**Table S1**). In particular, deconvolution of the peaks neither provides differences in surface hydroxylation (from the O1s peak) nor clear presence of Ti^{3+} states (from the Ti2p peak). This indicates that the created Ti^{3+} states that lead to darkening are beyond the detection limit of XPS. Another reason for the lack of detectability of Ti^{3+} in XPS, is re-oxidation of surface Ti^{3+} that is quite fast when samples are exposed to ambient air (as well documented in the literature).^[11,25]

Figure 2g,h show photoelectrochemical measurements carried out with a set of NT samples on the underneath Ti metal. For all samples studied, the photocurrent spectra show an onset of the photocurrent at wavelengths <380 nm, which corresponds to an indirect band gap (**Figure 2h**) of 3.05 eV. Therefore it can be deduced that UV illumination does not change the photoelectrochemical band gap, even though in absorption spectra (**Figure 1f**) an increase in the visible light range is observed. In other words, in reduced TiO_2 electronic states are generated that lead to visible light absorption but these states do not significantly contribute to a photocurrent. This may be explained by a limited mobility of the charge carriers generated by visible light - they remain trapped and then recombine.

Nevertheless, the magnitude of the photoresponse in the UV increases after illumination, which can be ascribed to a higher conductivity in the tubes^[11,26], caused by the light-induced defects. In order to characterize defect states and the formation of Ti^{3+} in-situ electron paramagnetic resonance (EPR) spectroscopic measurements were carried out. That is, in-situ EPR measurements with powder samples were taken during illumination (**Figure 3a,b**; see also Supporting information **Figure S3** and **S4** for details on the data evaluation). For these measurements, nanopowder slurries were placed in quartz EPR tubes, using O_2 -free solutions (50 vol% of methanol) at 95 K. EPR spectra were recorded for different illumination times. The measurements of pristine TiO_2 powder (**Figure 3a**, 0 h) show a low-intensity, sharp EPR signal centered at $g = 2.01$. This resonance is assigned to natural $\text{Ti}^{3+}/\text{O}_\text{v}$ defects in anatase,

where EPR-active Ti^{3+} is present on regular lattice positions.^[14] Illumination of the slurry leads to notable changes in the EPR resonance. In addition to the low-intensity signal, a second, significantly more intense isotropic EPR signal, centered at a g-value of $g = 1.93$, is detected unambiguously (**Figure 3 a,b**).^[12] With increasing illumination time, the intensity of the absorption at $g = 1.93$ increases considerably (**Figure 3b**). Note that the Y-scale in **Figure 3b** is 2 times attenuated (fully integrated signal intensities are given in **Figure S5**). This signal at $g = 1.93$ can be assigned to Ti^{3+} in an amorphous or distorted lattice.^[12] Most importantly, its resonance position and shape is similar to previously reported Ti^{3+} spectra in grey titania that are equally suitable to provide electron transfer mediation to promote H_2 generation.^[11] In other words, not only externally generated Ti^{3+} sites (*via* chemical reduction with H_2) but also light-induced Ti^{3+} states enable an activating path for H_2 evolution.

In-line with these findings, *in-situ* impedance measurements (**Figure 3c**, details are described in the experimental section), taken during illumination of the nanotube layers at different times, show a steady decrease of the charge transfer resistance R_{ct} . This reflects the facilitated electron transfer across the $\text{TiO}_2/\text{H}_2\text{O}$ interface. Overall, the *in-situ* data thus show that UV illumination of anatase triggers the formation and steadily increases the concentration of energetically suitable Ti^{3+} states that are beneficial for charge transfer and photocatalytic H_2 evolution. We believe that this autocatalytic process driven by solar or UV light has significant implications. On one hand, it opens up a simple one-pot approach for co-catalyst free H_2 generation. On the other hand, these light modifications in titania during illumination also stress that data obtained from semiconductor photocatalysis need to be carefully assessed, as the effect described here may significantly overlap or interfere with a straightforward data evaluation, when other parameters of catalytic effects are studied.

Overall, the present work clearly shows that illumination of TiO₂ nanopowders and NTs can induce a noble-metal-free and external-bias-free photocatalytic H₂ production in neutral aqueous solutions containing methanol.

Furthermore, one may conclude that the main effect of UV illumination, except for the well-described photochromic effect, is the formation of Ti³⁺ states that are energetically suitable for mediating photoelectron transfer to the aqueous environment.

Particularly fascinating is the observed self-amplification, i.e. the bi-functional effect of light that first triggers the formation of co-catalytic states that then increasingly causes an enhanced H₂ evolution.

The intrinsic activation here demonstrated is of considerable scientific impact, as it opens up the possibility to *in-situ*, simply by light, activation of TiO₂ for noble-metal-free H₂ generation. Moreover, the large number of unresolved factors, such as the geometry of the substrates, or overlaying strategies for dopant and defect engineering, provide numerous possibilities and promising pathways to further improve this autocatalytic approach to photocatalysis.

Experimental Section

Anatase powder samples were purchased from Sigma Aldrich, purity: 99.8%, particle size: 25-35 nm. TiO₂ nanotubes were prepared by self-organizing anodization of a Ti substrate (Advent, 0.125 mm thickness, purity 99.6 +%). Before anodization the titanium substrates were degreased by sonication subsequently in acetone and ethanol, followed by rinsing with deionized water and drying in a nitrogen stream. Anodization was carried out in ethylene glycol-based (Sigma–Aldrich) electrolyte consisting of DI water (1M) and NH₄F (0.2 M, Sigma–Aldrich, 98%) for 20 min at 60 V using a power supply (VOLTRAFT VLP2403Pro) and a two-electrode cell with a platinum counter electrode. Thermal annealing was performed

in a furnace (Heraeus) in air at 450 °C for 1 h to convert the amorphous nanotubes layer to anatase.

For open circuit photocatalytic H₂ evolution measurements, 2 mg powder were dispersed into an oxygen-free aqueous methanol (50 vol. %) solution to prepare a suspension in a quartz tube. The suspension was illuminated either under AM1.5 solar simulator (100 mW/cm²) or a 365 nm LED (90 mW/cm²), respectively. Sampling was taken every 3 hours at the initial stage from the gas in the head space of the septum sealed quartz tube. A gas chromatograph (GCMS-QO2010SE, SHIMADZU) with TCD detector was used to measure the amount of H₂ generated. For nanotubes, the annealed anodic TiO₂ layer was immersed in the same electrolyte as the nanoparticle system. The sampling of gas from head space is also adopted from above experiments. Cycling experiments were conducted for anatase powder. GC measurements of produced H₂ volume were repeated every 3, 6, 9, and 24 hours after exposure to UV 365 nm illumination. Cycles were repeated three times, separated by 30 min purge with N₂ to remove the H₂ from the system and avoiding contact with air. To evaluate the effect of different light intensities on H₂ evolution fresh powder samples were exposed to UV illumination and GC measurements were applied to determine the generated H₂ after 3, 6, 9, and 24 hours. The intensities were adjusted by controlling the 90 mW/cm² LEDs to 10% 50% and 200% intensity. Photoelectrochemical characterization was carried out with an electrochemical setup that consisted of a classical three-electrode configuration with an Ag/AgCl reference electrode and a Pt plate as a counter electrode. The illumination part of the setup consists of a 150 W Xe arc lamp (LOT-Oriel Instruments) as the irradiation source and a Cornerstone motorized 1/8m monochromator. The monochromized light was focused to a spot of 5×5 mm² onto sample surface (through a quartz light-pass window in the electrochemical cell). Photocurrent spectra were measured in 0.1 M (Na₂SO₄) at 500 mV (Ag/AgCl). Photocurrent transients were acquired

at each wavelength and the steady state photocurrent was determined. Photocurrent transients were recorded for 20 s with an electronic shutter system and A/D data acquisition.

Electron Paramagnetic Resonance (EPR) spectra were recorded on a JEOL continuous wave spectrometer JES-FA200 equipped with an Xband Gunn diode oscillator bridge, a cylindric mode cavity and a N₂ cryostat. The samples were measured in the solid state under argon atmosphere in quartz glass EPR tubes at 95 K with a similar loading of $\approx$ 20 mg. The EPR quartz tubes with samples and electrolyte were irradiated under AM1.5 solar simulator condition for different time intervals (same time scale with H₂ sampling). The spectra were measured with following parameters: Temperature 95 K, microwave frequency ν = 8.959 GHz, modulation width 1.0 mT, microwave power 1.0 mW, modulation frequency 100 kHz and a time constant of 0.1 s. Data analysis and simulation was carried out using the software “eview” and “esim” written by E. Bill (MPI for Chemical Energy Conversion, Mülheim an der Ruhr).

An X-ray photoelectron spectrometer (XPS, PHI 5600 XPS spectrometer, US) was used for compositional analysis of the samples. All XPS spectra were shifted to Ti2p peak at 458.00 eV. All samples were transferred from reaction quartz tube to the XPS stage in an argon atmosphere. The deconvolution of XPS spectra was performed using CasaXPS software.

The reflectance of the samples was measured between 300-600 nm in argon atmosphere (Avantes, AvaLight-DH-S-BAL, using cable IC-DB26-2). The reflectivity spectra were obtained in the reaction quartz tube and the blank quartz tube was used as reference. A Teflon standard was used as background.

The morphologies of the as-synthesized samples were characterized by a field emission scanning electron microscope (Hitachi S4800). Transmission electron microscopy was carried out with a Philips CM30 TEM. Geometrical features were measured from TEM images using Image J software.

XRD patterns of the crystallized powders were collected using an X-ray diffractometer (X'pert Philips PMD diffractometer) with a Panalytical X'celerator detector and CuK α radiation ($\lambda=1.54056$ Å).

Electrochemical Impedance Spectroscopy (EIS) measurements were performed using a computer controlled Zahner Zennium (ZAHNER-elektrik GmbH & Co. KG, Germany) potentiostat and a three-electrode quartz cell filled with oxygen-free 0.1 M NaSO₄ solution of H₂O and methanol mixture (3:1 vol.). The working area of the test material was defined as 1 cm²; the counter and reference electrodes were platinum and silver/silver chloride (Ag/AgCl in 3 M KCl), respectively. The measurements were carried out at open circuit potential (OCP) established before each measurement. To confirm the changing electrode properties after light illumination (Ti³⁺ - O_v formation), the EIS measurements were conducted under illumination after different exposure times (0, 3, 20, 44 h) of the sample surface with 365 nm LED (90 mW/cm²). Measurements were carried out over a frequency range from 100 kHz to 5 mHz, using a 10 mV amplitude sinusoidal signal.

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Figure 1. Volume of generated H₂ on: a) 2 mg of anatase powder in 10 mL H₂O: methanol (50:50 vol.%) and b) TiO₂ nanotubes after 1h annealing in 10 mL H₂O : MeOH (50:50 vol.%). c) Cycling experiment of photocatalytic H₂ evolution on anatase powder under UV 365 nm light. d) Photocatalytic H₂ evolution on anatase powder during illumination with 10%, 50% and 200% of UV lamp intensity, measured after 3h, 6h, 9h, 24h. e) Photography illustrating changes of anatase powder color after varied time of illumination with AM 1.5: (from the left side) 0h, 3h, 10h, 24h, 40h. f) Reflectance spectra of anatase powder slurries after 0 ~ 40 h of illumination with AM 1.5.

Figure 2. SEM images of illuminated a) anatase powder, and b) TiO₂ nanotubes. XRD patterns before/after UV irradiation on c) anatase powder and d) TiO₂ nanotubes. e,f) XPS data of anatase powder before and after UV illumination. g) IPCE results of nanotubes before and after 48 h illuminated with UV lamp. h) Evaluated bandgap from IPCE data (g).

Figure 3. EPR spectra of anatase powder after varied time of illumination with AM 1.5: a) for 0 and 3 h, and b) 10, 24, and 40 h. Please note that in b) the intensity is attenuated by a factor of 2. c) Nyquist plot of electrochemical impedance spectroscopy (EIS) data taken for TiO₂ nanotubes before (0h) and after illumination (3h, 20h, 44h).

TOC: The work shows that illumination of TiO_2 nanopowders and nanotubes not only leads to a continuous darkening due to $\text{Ti}^{3+}\text{-O}_v$ formation but also shows that these states activate photocatalytic hydrogen generation from neutral aqueous solutions. Steadily increasing Ti^{3+} formation goes hand-in-hand with an increase in H_2 evolution.