Critical factors for photoelectrochemical and photocatalytic H\textsubscript{2} evolution from gray anatase (001) nanosheets

Shanshan Qin\textsuperscript{1,5}, Nikita Denisov\textsuperscript{1,5}, Xin Zhou\textsuperscript{1}, Lukáš Zdražil\textsuperscript{1}, Dominik Fehn\textsuperscript{1}, Imgon Hwang\textsuperscript{1}, Mark Bruns\textsuperscript{1}, Hyesung Kim\textsuperscript{1}, Karsten Meyer\textsuperscript{3} and Patrik Schmuki\textsuperscript{1,2,4,}\textsuperscript{*}

\textsuperscript{1} Department of Materials Science WW4-LKO, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Martensstrasse 7, 91058 Erlangen, Germany
\textsuperscript{2} Regional Centre of Advanced Technologies and Materials, Šlechtitelů 27, 78371 Olomouc, Czech Republic
\textsuperscript{3} Department of Chemistry and Pharmacy, Inorganic and General Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 1, 91058 Erlangen, Germany
\textsuperscript{4} Department of Chemistry, Faculty of Science, King Abdulaziz University, PO Box 80203, Jeddah 21569, Saudi Arabia
\textsuperscript{5} Contributed equally to this work.
\textsuperscript{*} Author to whom any correspondence should be addressed.

E-mail: schmuki@ww.uni-erlangen.de

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Abstract

In recent years, the defect engineering of titania via reduction treatments has shown a high potential for enabling efficient and co-catalyst-free photocatalytic H\textsubscript{2} generation from methanol/water solutions. However, defect engineering simultaneously alters several properties of TiO\textsubscript{2}. Here, we use pristine (white) and hydrogenated (gray) anatase nanosheets with dominant (001) facets. By comparing electrical conductivity, photocurrent spectra, transient photocurrent response, and photocatalytic H\textsubscript{2} evolution, we show that the increased conductivity or broad visible light absorption of gray titania is not responsible for its increased activity. Instead, the true bottleneck is the hole transfer rate that is significantly accelerated while using gray instead of white modification. Moreover, the hole transfer reaction causes the accumulation of the reaction products in pure water, hindering the photocatalytic H\textsubscript{2} evolution over time. These combined factors explain the superior performance of gray titania over white titania in photoelectrochemical or photocatalytic water splitting.

1. Introduction

The increasing global energy demand (annual growth rate of \(\sim\)1.4% estimated until 2035)\textsuperscript{[1]} spurred by economic growth expectations puts an enormous stress on Earth’s limited energy resources (e.g. fossil fuels) and poses potential environmental risks (such as acid rain or the greenhouse effect)\textsuperscript{[2]}. Therefore, scientific attention has been directed widely toward finding renewable and environmentally friendly energy sources. Following the discovery of the photovoltaic effect in 1839 by Edmond Becquerel\textsuperscript{[3]}, massive efforts have been focused toward the development of solar energy harvesting technologies. A particularly attractive way of utilizing solar energy is provided by photoelectrochemical and photocatalytic processes; they allow a direct conversion of solar energy via water splitting to produce hydrogen (H\textsubscript{2}) from aqueous environments\textsuperscript{[4, 5]}. Early observations of the photoelectrochemical water splitting were made in 1972 by Fujishima and Honda using titania (TiO\textsubscript{2}) as a light-absorbing semiconductor\textsuperscript{[6]}. Since then, despite the discovery of many other suitable semiconductors, TiO\textsubscript{2} in its various forms (e.g., anatase, rutile, brookite, or TiO\textsubscript{2}-B) has acquired a research interest that is second to none in both photoelectrochemical and photocatalytic applications. This is mainly attributed to low costs, non-toxicity, chemical inertness, and outstanding photocorrosion resistance of TiO\textsubscript{2}\textsuperscript{[7]}. Being an intrinsic n-type semiconductor, it also offers a remarkable electron mobility\textsuperscript{[8]} and long electron lifetime (>1 \(\mu\)s in anatase)\textsuperscript{[9]}, allowing an electron diffusion length of up to several hundred...
micrometers [10]. Most importantly, the band-edge positions in TiO\textsubscript{2} allow it to decompose H\textsubscript{2}O into H\textsubscript{2} and O\textsubscript{2}, as well as •OH radicals [11].

However, despite the favorable thermodynamics for overall water splitting, pristine (i.e., stoichiometric) TiO\textsubscript{2} phases still show underwhelming H\textsubscript{2} evolution rates from pure water [12, 13]. This is most commonly ascribed to high overpotentials for driving surface reactions due to the sluggish migration and transfer of photogenerated charges, as well as undesired recombination processes in TiO\textsubscript{2} [14–16]. Therefore, various strategies have been developed to overcome the intrinsic performance limitations of TiO\textsubscript{2}. Methanol is often used as a sacrificial agent to ensure a swift scavenging of the photogenerated holes (owing to a more negative redox potential than H\textsubscript{2}O [17]) and prevent their recombination with electrons. Other measures to accelerate the reaction kinetics include surface decoration with noble metal co-catalysts to create Schottky junctions [18], forming heterojunctions with other semiconductors or between different TiO\textsubscript{2} phases [19], doping with various elements [19], tuning the structural properties (e.g., via maximizing the effective surface area [20–23], or creating specific crystal facets) [24] or utilizing, as mentioned above, sacrificial reagents (e.g. hole scavengers) to aid electron–hole separation [25–27]. Only recently, following the discovery of ‘black’ TiO\textsubscript{2} by Chen and Mao in 2011 [28–31], defect engineering rose to prominence as an effective approach to modifying the electronic properties of TiO\textsubscript{2} in a favorable way for photocatalytic applications. In particular, subjecting TiO\textsubscript{2} to different reductive (e.g., high-temperature oxygen-deficient) conditions allows to introduce intrinsic defects into its lattice, causing a color change of TiO\textsubscript{2} (‘gray’, ‘blue’, or ‘black’) corresponding to the degree of reduction. The appearance of a gray or black to blue color can be ascribed to Ti\textsuperscript{3+} and O\textsubscript{2} species that increase in concentration with an increasing level of reduction. The origin of such colors is typically assigned to the interband states introduced by reduction [32, 33]. These differently colored TiO\textsubscript{2} modifications exhibit a remarkably enhanced performance in co-catalyst-free H\textsubscript{2} evolution [34–40].

The mechanism of photocatalytic activity enhancement in reduced TiO\textsubscript{2} has been discussed extensively. From the comparison of mildly reduced (gray) and strongly reduced (black) TiO\textsubscript{2} specimens, it was clearly shown that stronger visible light absorption (i.e., a seemingly narrowed band gap) [28, 29, 35] and higher electrical conductivity of black TiO\textsubscript{2} offer (without additional Pt co-catalyst) presented no apparent advantage to the photocatalytic performance [36]. It was further proposed that the activity is not directly related to generally high Ti\textsuperscript{3+} content, but instead to an optimized content of a specific type of co-catalytically active defects (Ti\textsuperscript{3+}_\textsubscript{surface}) in hydrogenated gray TiO\textsubscript{2}, which provide kinetically beneficial mediator states for electron transfer to electrolyte [34–36, 41–44]. In addition to electron transfer, more efficient hole utilization by reduced TiO\textsubscript{2} has also been proposed to be due to a drastically prolonged lifetime of shallow-trapped and deeply trapped photogenerated holes in gray anatase [30]. Accordingly, density functional theory (DFT) calculations [45] have also suggested a strong localization of holes in the disordered surface layer of hydrogenated TiO\textsubscript{2}. It has also been suggested that subsurface interstitial Ti atoms in reduced TiO\textsubscript{2} may affect its interaction with liquid-phase species (e.g., by changing activation energy barriers or providing additional reaction pathways) [34, 46], which could lead to accelerated charge transfer kinetics.

Overall, a broad spectrum of possible changes to TiO\textsubscript{2} properties can be induced by reductive treatments. Identifying their individual contributions to the photocatalytic and photoelectrochemical performances of white and gray TiO\textsubscript{2} is of utmost importance to advance TiO\textsubscript{2}-based water splitting processes.

Therefore, in the present work, we elucidate several critical factors in the photocatalytic performance of white and gray anatase TiO\textsubscript{2}. We investigate conductivity, incident photon-to-current conversion efficiency (IPCE), transient photocurrent response, and photocatalytic H\textsubscript{2} evolution activity of white and gray anatase nanosheets (NSs) enriched with (001) facets in pure water and methanol containing solutions. We show that the hole transfer rate in aqueous solutions is the main factor limiting the H\textsubscript{2} generation in the performance of TiO\textsubscript{2}. Hole transfer limitations are strongly alleviated in the gray modification of TiO\textsubscript{2}, showing a remarkably enhanced photocatalytic H\textsubscript{2} evolution and photocurrent generation in aqueous solutions compared to white titania. Furthermore, we find a decay of the photocatalytic performance over time in pure water, which is ascribed to the formation of surface-bound Ti-peroxo-species that significantly hamper the reaction rate.

2. Experimental section

2.1. Synthesis of anatase TiO\textsubscript{2} NSs

TiO\textsubscript{2} NSs were synthesized following the reported methods [47]. A hydrothermal method with commercial reagents of titanium (IV) butoxide (Ti(OBu)\textsubscript{4}, 97%) from Sigma-Aldrich and hydrofluoric acid (HF, 48%) from Carl Roth were used for synthesizing NS. In a typical synthesis procedure, 1.2 ml of HF was added dropwise to 10 ml of Ti(OBu)\textsubscript{4} under stirring at room temperature that was placed in a 250 ml Teflon liner. Before the mixture solution was sealed in an autoclave, the stirring continued for the next 40 min. The solution was eventually transferred to a preheated oven at 250 °C+. The reaction was completed after 24 h, and the autoclave was allowed to cool naturally in the oven. After the hydrothermal reaction, the precipitates
were collected and washed thrice with ethanol and distilled water each, then dried in the oven at 70 °C for 12 h.

As-synthesized (As-NS) TiO$_2$ anatase NSs were annealed in air at 500 °C for 1 h. The sample is annotated 500A-NS. After air annealing, the obtained samples were hydrogenated in a pure H$_2$ (Linde, 99.99%) flow at 500 °C for 1 h with a pressure of 20 bar. After a two-step thermal treatment, we obtained samples 500A-500H-NS. The as-synthesized TiO$_2$ anatase NSs were annealed in pure H$_2$ or air at 500 °C for 1 h to obtain the samples of 500H-NS or 500A-NS, respectively.

2.2. Photoelectrochemical studies

Electrodes for photoelectrochemical characterization were fabricated using 0.2 mg of different annealed TiO$_2$ photocatalysts of NS in water/ethanol 50:50 Nafion slurry placed on a carbon electrode. The electrode was then placed in a three-electrode photoelectrochemical cell as a working electrode. An Ag/AgCl electrode was used as a reference electrode and a Pt plate as a counter electrode. A total of 1 M of Na$_2$SO$_4$ dissolved in distilled water or in H$_2$O: methanol = 80:20 vol.% solutions were used as electrolyte, and the applied potential was 0.5 V vs. Ag/AgCl. Illumination was provided by a 150 W of the Xe arc lamp (LOT-Oriel Instruments) with a Cornerstone motorized 1/8 m monochromator. The monochromized light was focused on a 5 × 5 mm$^2$ spot onto the sample surface through a quartz light-pass window in the electrochemical cell. At each wavelength, a photocurrent transient was acquired, and a steady-state photocurrent was recorded. Photocurrent transients were recorded for 20 s using an electronic shutter system and A/D data acquisition.

To characterize the performance of differently treated NSs, IPCE is characterized. In the case of photoelectrochemical water splitting, IPCE describes the maximum possible efficiency with which incoming radiation can produce hydrogen from water (assuming that all electrons are used for the hydrogen evolution) [44] and can be calculated as follows:

$$\text{IPCE} \, (%) = \left( \frac{I_{ph} \times \lambda}{I \times \lambda} \right) \times 100$$  \hspace{1cm} (1)

where $I_{ph}$ (mA cm$^{-2}$) is the photocurrent density, $h\nu$ (1240 eV nm$^{-1}$) is the photon energy of the incident light, $I$ (W cm$^{-2}$) is the irradiance of the electrode surface, and $\lambda$ (nm) is the wavelength of the light.

2.3. Photocatalytic H$_2$ evolution experiment

In a typical experiment, 2 mg of TiO$_2$ photocatalyst was dispersed in a 10 ml mixture of water and methanol (50:50 vol.%) solution (or 10 ml of DI water) in a quartz tube. After purging Ar for 20 min and its ultrasonic treatment for 10 min, the quartz tube was sealed, and the suspension was illuminated by a 365 m LED (95 mW cm$^{-2}$ in the case of methanol containing solution or 300 mW cm$^{-2}$ for pure water splitting) for 4 h under continuous stirring. A gas chromatograph (GC: GCMS-QQ2010SE, Shimadzu) with thermal conductivity detector was used to measure the amount of generated H$_2$. The sample was continuously stirred during irradiation, and GC measurements were conducted to evaluate the amount of generated H$_2$.

2.4. Characterization

The morphology of the samples was investigated by a field-emission scanning electron microscope (S-4800, Hitachi, Japan). Further information on morphology was assessed using high-resolution transmission electron microscope (HR-TEM, CM 30 TEM/STEM, Philips). The chemical composition of the samples was studied by x-ray photoelectron spectroscopy (XPS, PHI 5600), and all XPS spectra were calibrated with the Ti 2p peak up to 458.5 eV. Solid-state electrical conductivity measurements were conducted using a two-point probe configuration with a current source (Keithley 6221) and a nanovoltmeter (Keithley 2182). Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL continuous wave spectrometer JES-FA200, which was equipped with an X-band Gunn diode oscillator bridge, a cylindrical mode cavity, and a helium cryostat. The samples were measured as a solid (6 mg loading) in quartz glass EPR tubes at 95 K. The spectra shown were measured using the following parameters: microwave frequency = 8.959 GHz, modulation width = 1.0 mT, microwave power = 1.0 mW, modulation frequency = 100 kHz, time constant = 0.1 s.

Data analysis and simulation of the data was performed using the software ‘eview’, written by Dr Eckhard Bill (MPI CEC, Mülheim/Ruhr) [48]. Time-resolved photoluminescence (PL) spectroscopy measurements were conducted on FLS980 fluorescence spectrometer (Edinburgh Instruments) equipped with a picosecond pulsed diode laser EPL-375 (Edinburgh Instruments, $\lambda_{em} = 372$ nm with a pulse width of 66, 5 ps, a repetition rate of 10 MHz). The PL decays were fitted with a triple exponential function. To measure the electronic conductivity, a 200 nm Pt film as a conductive electrode was deposited on the surface of Si/SiO$_2$ wafer by a plasma sputtering machine (EM SCD 500, Leica). The electrical resistance is calculated as follows:

$$\rho \, (\Omega \cdot \text{cm}) = \frac{U}{I \times A/l}$$  \hspace{1cm} (2)
where $U$ (V) is the applied voltage, $I$ (A) is the obtained current, $A$ ($0.00001 \times 0.00001$ cm$^2$) is the top-side surface area of the NS, $l$ ($6 \times 10^{-7}$ cm) is the thickness of the NS.

3. Results and discussion

The morphology of the TiO$_2$ powders after hydrothermal synthesis and annealing in different atmospheres (air, H$_2$, or air followed by H$_2$) was studied by an HR-TEM, and the results are shown in figure 1. Both as-formed and annealed powders exhibit a NS structure with a crystalline lattice spacing of 0.352 nm, which corresponds to the distance between the (101) lattice planes in anatase [49, 50]. Additional TEM images of the NS taken from a perpendicular angle (figure S1) further confirm the (001) orientation of the dominant surface facets, as they are parallel to (001) lattice planes in the bulk of the NS. In contrast to black TiO$_2$ materials, which commonly exhibit an amorphous outer shell, this feature is not observed for gray titania because of a lesser degree of disorder introduced under milder hydrogenation conditions. Based on the previous reports [47], the large area facets exhibit (001) orientation due to the selective F-termination of (001) surfaces during hydrothermal growth. Additional SEM characterization (figure S2) confirms the as-formed structure of the NS to be well preserved during air- or two-step (air + H$_2$) annealing, whereas one-step H$_2$ annealing (500H-NS) leads to an apparent deformation/sintering of the NS.

EPR spectroscopy was conducted to explore the electronic nature of the defects introduced by the different treatments (figure S3). In contrast to the other samples, the as-synthesized NSs show a broad signal at $g_{\text{avg}} \approx 1.86$. Due to the presence of TiOF$_2$ in the as-synthesized NSs (figure S4), the broad signal at $g_{\text{avg}} \approx 1.86$ is related to defect interactions with F [49]. After annealing in air at 500 °C, a typical signature of Ti$^{3+}$ defects in a lattice of anatase (Ti$^{3+}_{\text{lattice}}$) can be detected [34, 49]. Upon hydrogenation, an additional defect signature becomes apparent (Ti$^{3+}_{\text{surface}}$ at 330–380 mT with a $g_{\text{avg}} \approx 1.93$) [34, 49]. A small signal at $g = 2.002$ is observed for either air- or H$_2$-treated samples, which corresponds to oxygen vacancies in the TiO$_2$ lattice [34, 51]. Introduced by hydrogenation, the Ti$^{3+}$ defect is located close to the conduction band of TiO$_2$ that serves as the electron transfer mediator for photocatalytic H$_2$ evolution or photoelectrochemical processes.

To elucidate the effect of the above thermal treatments on the electrical properties of the NS, we performed solid-state conductivity measurements for a single NS using a two-point method illustrated in figure 2(a). The recorded $I$–$V$ curves (showing forward and reverse polarizations) are presented in figure 2(b), and the corresponding resistivity is calculated in figure 2(c). The conductivity of the NS shows a slight increase after air-annealing, whereas a drastic increase is achieved by a two-step annealing treatment (air followed by H$_2$) and in a lesser degree by a one-step hydrogenation. Correspondingly, the resistivity drops by >120 times after a two-step annealing and by >70 times after one-step H$_2$ annealing. This indicates that Ti$^{3+}$ states and oxygen vacancies introduced via hydrogenation act as electron donors (as widely confirmed in the literature) [33, 34, 44, 52, 53], leading to an increased electrical conductivity of reduced TiO$_2$ as compared to pristine TiO$_2$ [29, 36]. Notably, resistivity changes are not related with the structural-phase transformation because only the anatase phase is observed for the NS that is thermally treated at different conditions in x-ray diffraction (XRD) (figure S4).

The content of fluoride remaining on the NS surface after hydrothermal synthesis and annealing procedures was studied by XPS, and the corresponding XPS spectra of the F 1 s region are shown in figure 2(d) (survey spectra are given in figure S5). The as-formed NS clearly shows an F 1 s signal at 684 eV, indicating the presence of surface F-termination [49]. After thermal treatment, the F 1 s peak can no longer be detected, indicating a complete removal of F.

The XRD patterns for the NS thermally treated at different conditions are shown in figure S4. All samples exhibit nearly identical XRD patterns corresponding to a pure anatase phase. The dominant peak at $2\theta = 25.3^\circ$ corresponds to the diffraction from the anatase (101) lattice planes (JCPDS No. 21-1272). Notably, the as-formed NS additionally shows a weak diffraction peak at $2\theta = 23.6^\circ$ corresponding to the TiOF$_2$ phase (JCPDS No. 08-0060). In line with XPS, this outcome points out that the F-species remain in the NS after the synthesis, which are further removed via thermal treatments.

To compare the hole transfer processes from white and gray titania in aqueous environments, we fabricated electrodes and measured their IPCE performance (figures 3(a) and (b)) in a three-electrode setup at a constant anodic bias of 0.5 V (vs. Ag/AgCl) in 0.1 M of Na$_2$SO$_4$ aqueous electrolytes, and the recorded spectra are shown in figure 3(a). Photocurrent densities corresponding to peak IPCE values for the NS annealed in different atmospheres are additionally provided in table S1. Under anodic bias solely hole transfer occurs at a TiO$_2$ photoanode, without any interference from the electron transfer (which proceeds at the Pt counter electrode [cathode]). Furthermore, electron depletion at anodic bias provides electron–hole separation and hole transport to the semiconductor/liquid interface. As a consequence, the photocurrent magnitude in the IPCE spectra in figure 3(a) reflects the hole transfer rate to the electrolyte under these conditions.
Figure 1. (a)–(d) HR-TEM images of (a) as-formed NS, (b) 500A-NS, (c) 500A-500H-NS and (d) 500H-NS.

conditions. The obtained results (without the addition of a hole scavenger to water) show a strong dependence of the IPCE performance on the annealing conditions: 500A-500H-NS (2.21%) > 500H-NS (1.96%) > 500A-NS (1.25%) > NS (0.61%). Notably, all samples have shown similar crystallinity according to HR-TEM (figure 1), as well as previous XRD studies [49]. Therefore, an increased IPCE by air-annealed NS can be ascribed to improved hole transfer properties, due to the removal of surface F-termination at high temperature (figure 2(d)). Additional hydrogenation (500A-500H-NS) leads to a 1.77 times increase in IPCE (as compared to 500A-NS), reflecting a more efficient transfer of photogenerated holes to the electrolyte in these gray anatase samples, compared to the white material. This improved IPCE in hydrogenated anatase samples can be ascribed to an elongated hole lifetime reported in [30] or may alternatively be related to an overall faster water oxidation kinetics, e.g., due to lowered activation energy barriers for hole-induced surface reactions (i.e., hole transfer) [54]. Also, surface adsorption effects can be influenced by various defect types (e.g., subsurface interstitial Ti or surface oxygen vacancies) in reduced TiO$_2$ (e.g., by providing active sites for adsorption and reaction) [34, 46, 55].

To further clarify the role of hole transfer kinetics in the performance of white and gray anatase, we measured their IPCE in the presence of a sacrificial hole scavenger (20 vol.% methanol), as shown in figure 3(b). Most remarkable, for the methanol containing solutions, a nearly identical IPCE performance at 3.4%–3.7% is observed for all samples regardless of their thermal treatment procedure, in stark contrast to the pure water case (figure 3(a)). This result indicates the main hole utilization bottleneck in white anatase is the hole transfer rate (i.e., sluggish water oxidation kinetics on white TiO$_2$). Hence, several other factors, such as differences in conductivity (figure 2(c)), electronic properties (e.g., electron donor density) or light absorption between white and gray TiO$_2$ NSs apparently have little to no influence on the performance, in line with some publications in the literature [36]. In turn, for methanol containing solutions the rate limiting
Figure 2. (a) SEM images of the conductivity measurement procedure. The inset shows isolated TiO$_2$ NS on the surface of Pt layer. (b) Solid-state conductivity measurements and (c) corresponding calculated electrical resistivity for as-formed NS, 500A-NS, 500A-500H-NS and 500H-NS. (d) XPS spectra in F1s region for TiO$_2$ NS thermally treated in different conditions.

The step is no longer material specific, i.e., the hole transfer step is not limited by distinct electronic states in the TiO$_2$ or charge transfer mediator in these states. These observations may be key to many observations in the literature, such as material rankings that switch order when measurements are performed for different electrolytes or photocatalytic carrier capture systems [56].

IPCE spectra were further used for the bandgap evaluation of the TiO$_2$ NS (figures 3(c) and (d)). It shows small variations in the range of 3.2–3.3 eV, in line with the reported $E_g$ values for the anatase phase of TiO$_2$ (3.2 eV). In line with previous reports [57], the enhanced visible light absorption by reduced TiO$_2$ does not actually lead to a commensurable photocurrent generation in the visible spectral range, e.g., due to an insufficient mobility of the photocarriers trapped on sub-band gap states [36, 44, 58].

The transient photocurrent response at $\lambda = 325$ nm from the as-formed NS, 500A-NS, 500A-500H-NS and 500H-NS electrodes is provided in figures 3(e) and (f). Because steady-state (i.e., after 20 s of illumination) photocurrent measurements were used to calculate IPCE values, they repeat the exact same trend as in figures 3(a) and (b). Notably, both in the absence (figure 3(e)) and presence (figure 3(f)) of methanol, all samples exhibit very similar transient photocurrent kinetics, which are dominated by processes significantly slower than the hole transfer. Slow photocurrent rise and decay (taking $\sim 10$ s in both cases) under alternating illumination typically indicates a sluggish electron transport through the electrode influenced by trapping/detrapping processes (particularly at the boundaries between individual NSs) [44, 59, 60].

The charge carrier recombination kinetics of pristine and treated TiO$_2$ NS was investigated using time-resolved PL spectroscopy (figure S6). The PL relaxation is characterized by a multiexponential decay, and the best fit of the decay is extracted from a triple-exponential function. As observable from figures S6 (b) and (c), thermal treatment of pristine TiO$_2$ NS in H$_2$ and air environment led to enhancement of average PL lifetime from 7.3 ns to 8.6 ns and 9.6 ns, respectively, indicating the passivation of surface states. In contrast, a noticeable decrease in the average lifetime of PL for the 500A-500H-NS sample was observed compared to
Figure 3. (a), (b) IPCE spectra for the as-formed NS, 500A-NS, 500A-500H-NS and 500H-NS electrodes measured at 0.5 V (vs. Ag/AgCl) in (a) 0.1 M of Na$_2$SO$_4$ aqueous electrolytes and (b) 0.1 M of Na$_2$SO$_4$ electrolytes containing 20 vol.% of methanol. (c, d) Evaluation of the band gap energy from the IPCE spectra (a) and (b), respectively. (e, f) Transient photocurrent response for the as-formed NS, 500A-NS, 500A-500H-NS and 500H-NS electrodes recorded under illumination at $\lambda = 325$ nm at 0.5 V (vs. Ag/AgCl) in (e) 0.1 M of Na$_2$SO$_4$ aqueous electrolytes and (f) 0.1 M of Na$_2$SO$_4$ electrolytes containing 20 vol.% of methanol.

the other thermally treated samples, indicating a more pronounced separation of excited charges leading to a higher photocatalytic activity of the sample [61].

To elucidate the importance of hole transfer in the open-circuit photocatalytic activity, we measured H$_2$ production by white and gray NSs under irradiation in a 50 vol.% methanol solution (power density of 95 Mw cm$^{-2}$ at $\lambda = 365$ nm) (figure 4(a)), or in pure DI water (power density of 300 mW cm$^{-2}$ at $\lambda = 365$ nm) (figure 4(b)). Here, the activity of the NS is also affected by the annealing treatments (500A-500H-NS > 500A-NS > 500H-NS > as-formed NS), while methanol provides a higher H$_2$ evolution performance due to a swift hole scavenging and photo-reforming reaction [62].

To account for the possible surface area changes induced by the thermal treatments and their effects on the photocatalytic performance of TiO$_2$ NS, mass-specific surface Brunauer–Emmett–Teller (BET) analysis was additionally performed. As shown in figure S7, thermal treatment of the as-formed NS has led to a decrease in their specific surface area by 2.8 times (500H-NS) or 1.3 times (500A-500H-NS). Thus, it can be
suggested that the benefits of hydrogenation treatment, such as tuning the electronic properties of TiO$_2$ to allow efficient electron transfer, apparently outweigh the negative effects of surface area reduction in the overall performance of hydrogenated NS.

However, in contrast to IPCE measurements (figure 3(b)), the performance is not equalized by the addition of a hole-scavenging agent. Also, no direct correlation of the H$_2$ evolution performance of the NS with their conductivity can be observed. Most importantly, because both reduction and oxidation reactions occur at the same particle, the performance depends on hole transfer and electron transfer to the liquid phase, which can assist in determining the rate.

In this situation, i.e., for the gray material in methanol solution, the electron transfer mediating states (widely described in the literature) [34, 36, 49] seem to reflect the key factor for the overall H$_2$ evolution performance. Specifically, Ti$^{3+}$ defects introduced by hydrogenation are known to modify the electronic band structure of TiO$_2$ by forming energy states located below the conduction band, which are considered to provide efficient electron transfer during photocatalytic H$_2$ evolution. Accordingly, EPR studies of the intermediately reduced (‘gray’) TiO$_2$ indicate that the surface Ti$^{3+}$ states are mainly responsible for their...
superior H\textsubscript{2} evolution activity as compared to strongly reduce ('black') TiO\textsubscript{2} \cite{34, 49}. Please note that for the first time interval, the H\textsubscript{2} production rate from the methanol solution and plain water are virtually identical in this initial time for the gray material, if the hole transfer do not limit the overall performance. After this highly effective initial period, the photocatalytic performance levels off at a steady state that is remarkably stable.

As illustrated for the 500A-500H-NS sample in DI H\textsubscript{2}O (figure 4(c)), a decay in H\textsubscript{2} production rate can only be seen after 6 d of illumination. It is noteworthy that illumination does not change the structure of the NS by SEM (figure S8) and XRD (figure S9). More important and interesting, however, is the loss of photocatalytic activity under illumination in the initiation phase (only observed in pure water) has been previously reported for TiO\textsubscript{2} photocatalysts. Kiwi and Graetzel observed the saturation of H\textsubscript{2} evolution due to peroxide formation that irreversibly affect the catalyst \cite{63}. The oxidation of OH-groups by photogenerated holes has been ascribed to form surface-bound H\textsubscript{2}O\textsubscript{2} and consequently Ti-peroxocomplexes (or Ti–O–O–H), which can also react with photogenerated electrons, thus hindering the H\textsubscript{2} evolution \cite{63–65}. This effect has also been addressed in several previous studies, where a gradual decay of H\textsubscript{2} evolution was found to be due to Ti-peroxo-species formation on the TiO\textsubscript{2} surface \cite{63, 66–69}. This is supported by an almost linear H\textsubscript{2} evolution in the presence of a hole scavenging agent in figure 4(a) (i.e. methanol oxidation competes with the formation of peroxo-species), and also by the lack of observable O\textsubscript{2} evolution (monitored in the gas phase by GC) in NS samples (as widely reported in the literature) \cite{30, 70, 71}. In line with observations for NS, conventional anodic TiO\textsubscript{2} nanotubes similarly show only a short period of O\textsubscript{2} production (during the initial 1 h) followed by its complete suppression (figure S10), while a further O\textsubscript{2} consumption in the reaction medium suggests H\textsubscript{2}O\textsubscript{2} production via two-electron reduction of the produced O\textsubscript{2} \cite{64–66}.

4. Conclusions

The presented analysis of conductive properties, photocurrent generation, and photocatalytic H\textsubscript{2} evolution for white and gray anatase NSs clearly identifies the sluggish hole transfer to pure water (i.e. water oxidation reaction) as a significant factor limiting the performance of white titania in the solar energy conversion applications that rely on semiconductor-liquid junctions, such as photocatalysis for H\textsubscript{2} evolution from water. This limitation is overcome by gray titania by introducing Ti\textsuperscript{3+} defect states via suitable thermal treatment in air and H\textsubscript{2}, providing a remarkable photoanode material and a high co-catalyst-free photocatalytic performance. Nevertheless, an intrinsic feature of anatase TiO\textsubscript{2} in pure water splitting is the decay of H\textsubscript{2} evolution rate due to the surface accumulation of reaction products, such as Ti-peroxo-species, which remains a hurdle to be overcome.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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Conflict of interest

The authors declare that there is no conflict of interest.

ORCID iDs

Shanshan Qin \textcopyright https://orcid.org/0000-0001-7693-115X
Patrik Schmuki \textcopyright https://orcid.org/0000-0002-9208-5771
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