Electrochemically Faceted Bamboo-type TiO₂ Nanotubes Provide Enhanced Open-Circuit Hydrogen Evolution

Lei Ji,^[a,b] Xuemei Zhou,^[a] and Patrik Schmuki^{*[a]}

[a] Prof. Dr. Ji Lei, Xuemei Zhou, Prof. Dr. Patrik Schmuki, Department of Materials Science WW-4, LKO; University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany. Email: schmuki@ww.uni-erlangen.de.

[b] Prof. Dr. Ji Lei, College of Chemistry and Chemical Engineering, Northeast Petroleum University, 199 FaZhan Road, 163318 Daqing, China.

Link to the published article:

<https://onlinelibrary.wiley.com/doi/full/10.1002/celc.201800584>

Abstract: In this paper we prepare faceted “black” TiO₂ nanotube arrays (NTAs) with a bamboo-type structure which exhibits an enhanced performance for open-circuit H₂ generation without the use of any noble metal co-catalyst. By applying positive and negative voltages alternatively during electrochemical TiO₂ nanotube formation, not only a bamboo structure can be formed but tubes are reduced in the cathodic cycle. After a rapid annealing treatment of these tubes in air at 500 °C for 10 s, TEM shows that the bamboo rings (knots) provide (001) facets preferentially located at the knot, while (101) planes prevail on the smooth part of tube between knots. The short annealing time keeps co-catalytically active centers (Ti³⁺/oxygen vacancy (V_O)) still preserved in the TiO₂ NTAs. The results of intensity modulated photocurrent spectroscopy (IMPS) and open-circuit potential (V_{OC}) measurements indicate that these faceted and reduced TiO₂ nanotube arrays provide an efficient separation and reaction of photo-generated charge carriers, and this leads to an improved photocatalytic H₂ evolution performance.

Introduction

Titanium dioxide (TiO₂) is one of the most widely investigated semiconductors due to its intrinsic chemical and photochemical stability.^{[1]-[4]} The use of TiO₂ material as photocatalyst was pioneered in 1972 by Fujishima and Honda, who have reported photocatalytic water splitting (to H₂ and O₂) using a TiO₂ single crystal.^[5] Since then, the concept of using photocatalysts to convert solar light to chemical energy (stored in H₂) has attracted wide interest,^{[6],[7]} although the wide bandgap of TiO₂ (e.g. 3.0 eV for rutile and 3.2 eV for anatase) allows only for UV activation of a photocatalytic reaction.^{[8]-[10]}

For a photocatalytic approach, using TiO₂ under open-circuit potential (OCP), a main challenge is the slow charge transfer kinetics on TiO₂ (i.e. a hampered charge carrier transfer to the electrolyte and thus a dominant recombination of charge carriers). Therefore the photocatalytic generation of H₂ from aqueous solutions on pure TiO₂ does hardly occur, although it is thermodynamically permitted.

Conventionally this kinetic problem is tackled by decorating TiO_2 with suitable co-catalysts (noble metals such as Pt, Pd, Au etc.)^{[11]-[15]}. These noble metal co-catalysts act as charge transfer mediators for electron transfer from conduction band of TiO_2 to the electrolyte. However, this raises economic concerns regarding the use of costly noble metals for a “cheap” TiO_2 based-photocatalyst. Therefore, recent findings by Liu *et al.* on the preparation of “grey TiO_2 ” nanotubes^[16] or nanoparticles^[17] that by annealing treatments in high pressure H_2 at high temperatures generate a catalyst that produces hydrogen under open circuit conditions without the presence of any co-catalyst are noteworthy. These works proposed that specific and stable Ti^{3+} species can act as intrinsic co-catalytic centers in TiO_2 .^{[18]-[21]}

In order to facilitate charge separation in photocatalysts (except of charge transfer mediating noble metals or defects) also crystal faceting has been described as effective.^{[22]-[26]} In view of reduced TiO_2 , Liu *et al.*^[27] investigated the crystal facets of single crystal anatase and their photocatalytic activity for H_2 evolution under noble-metal-free conditions. They found that intact facets carrying Ti^{3+} centers were not active. If, however, these intact facets were damaged using scratching or ion-implantation, they show clear activity for H_2 production – the authors therefore concluded high index planes to be involved in the noble-metal-free activation.^[27]

An advanced morphology for photocatalytic and photoelectrochemical reactions are self-organized anodic titanium dioxide nanotube arrays (**TiO_2 NTAs**) that provide vertically oriented one-dimensional charge transport features, orthogonal charge separation characteristics, and a high specific surface area.^{[28],[29]} While faceting has been investigated for TiO_2 nanoparticles, it has hardly been explored on TiO_2 nanotubes.

In this work we explore the feasibility to prepare differently faceted bamboo tubes. Additionally we create reactive Ti^{3+} states embedded in these TiO_2 tubes by cathodic reduction.^{[30]-[32]} We show that both features, faceting and Ti^{3+} generation, can be induced by alternative oxidation/reduction growth of the tubes, followed by fast air annealing of the tubes. This modified TiO_2 NTA configuration in comparison to non-

faceted tubes shows a considerably enhanced activity for H₂ evolution under AM1.5 conditions, without the use of noble metal co-catalysts.

Results and Discussion

We prepared reduced bamboo-type NTAs as outlined in **Figure 1a** and as detailed in the experimental section by an alternating electrochemical growth/reduction treatment of a titanium substrate in NH₄F/H₂O/ethylene glycol electrolyte. First a number of parameters of anodic and cathodic cycling were screened, namely the duration of positive and negative voltages and their effect on morphology and photocatalytic activity investigations.

Examples of different morphologies after electrochemical growth are shown in the SEM images in **Figure 1b-d** and **Figure S1a-b**. The SEM image in **Figure 1c** represents a typical example of a tube prepared by 10-cycles of a potential stepping profile consisting of anodic polarization at 60 V for 150 s followed by -20 V for 150 s (denoted as PR-20-TiO₂ NTAs) – a detailed key to annotation of samples is given in **Table 1**. For PR-20-TiO₂ NTAs, clearly the presence of bamboo-like structures with regular intervals of the whole tube can be seen.

Figure 1. (a) Illustration of the growth of partially reduced bamboo-like TiO₂ NTs. (b-c) SEM images of PR-20-TiO₂ NTAs. (d) SEM image of NR0-TiO₂ NTAs.

It is noteworthy that during the negative voltage cycle, a fast electrochromic color change can be observed due to a Ti⁴⁺ to Ti³⁺ reduction/ion-insertion process.^{[33]-[36]} This process is reversible in color, i.e. in the negative cycle the color of TiO₂ NTAs changes from light brown to black while in the positive cycle it changes back to brown (due to re-oxidation of most of the Ti³⁺ to Ti⁴⁺).^{[33]-[36]}

From a closer observation, the thickness of a knot is about 50-100 nm (the inset image in **Figure 1c**), which corresponds to the thickness of a compact layer formed upon switching the voltage to a positive value (see **Figure 1a**).^[37] The space between knot structures can be controlled by the time interval of positive voltage, *e.g.* a narrower space can be obtained for the PR tube with 60 cycles (anodized at 60 V for 50 s, see **Figure S1a**). The relation between the length of space and duration of positive voltage is shown in **Figure S1c**. In order to evaluate the influence of the strong negative voltage pulse in comparison to a non-reductive pulse, we carried out a reference experiment where we – after the anodic pulses – only returned to 0 mV, i.e. with a sequence of 60 V for 150 s, then 0 V for 150 s (denoted as NR0-TiO₂ NTAs). In this case, the knot structure has a much smoother morphology (**Figure 1d**). This illustrates that the strongly reducing conditions also affect the knot morphology formed in the next anodic pulse.

After formation – ending always with a reductive pulse – the samples were annealed in air using Rapid Thermal Annealing (RTA) with a temperature increase rate of 1 °C/s and kept at 500 °C for 10 s. From a set of preliminary experiments we found that under

the annealing conditions, the materials can be crystallized but also remain partially reduced (i.e. Ti^{3+} species are maintained as shown later).

Characterization of different TiO_2 NTAs in view of their crystalline structure was carried out with X-ray diffraction (XRD) (**Figure 2a** shows some representative examples). The reduced TiO_2 NTAs before annealing are amorphous, and therefore show only diffraction peaks from the underlying metal Ti. After annealing typical diffraction peaks of anatase TiO_2 become apparent that can be indexed to the (101), (001), (200), (105), (211), (204), (116) crystal planes [identified using JCPDS data (21-1272)]. Since the peak for the (001) facet is overlapping with the Ti metal peak, we analyzed the intensity of anatase (101) peak compared with Ti substrate peak at 40.2° . From the comparison of relative intensities, one can deduce that for the reference TiO_2 NTAs, (101) planes are present in a significantly larger proportion than in tubes prepared after alternating reduction, where e.g. (001) facets show an increased relative intensity. This becomes more evident from high-resolution transmission electron microscopy (HRTEM).

HRTEM images for sample PR-20 TiO_2 NTAs are shown in **Figure 2b-c** and **Figure S2**. These images reveal that after annealing, at the knot zone, (001) facets with $d=0.237$ nm are preferentially present. They are perpendicular to the tube wall (**Figure 2b**) in contrast to the rest of the tube walls, where (101) planes are present (**Figure 2c**). Thus clearly the knot region in the annealing step is crystallizing with a different facet orientation than the rest of the tube.

Figure 2. (a) XRD patterns of amorphous PR-20-TiO₂ NTAs, annealed NR, PR-20 and FR TiO₂ NTAs (all peaks are normalized to the intensity of Ti as 2θ of 40.2°). (b-c) HRTEM images of PR-20-TiO₂ NTAs. (d) EPR spectra of NR, PR-20 and FR TiO₂ NTAs.

In order to investigate the presence of Ti³⁺ species, electron paramagnetic resonance (EPR) spectra were measured at 90 K in dark. As shown in **Figure 2d**, it is observed that the reduced TiO₂ NTAs give rise to two types of resonance signals, *i.e.* a notable EPR signal at $g \approx 1.998$ and a minor and broad signal at $g \approx 1.984$. These g -values have been attributed to different Ti³⁺ centers.^{[38],[39]} The former resonance signal is ascribed to Ti³⁺ ions located in regular lattice positions. These Ti³⁺ states generally form electronic states within the band gap and are responsible for visible-light absorption.^[40] While the small but apparent resonance line $g=1.984$ can be attributed to Ti³⁺ dislocated

from the regular position which reveals the lattice deformation trend. [refs] The signal at $g \approx 1.984$ of PR-20 TiO₂ NTs proportionally shows higher intensity comparable to that of FR-tube, that is, the lattice deformation structure of partially reduced bamboo-like sample is more severe.

Obviously, it can be seen that the intensity of this Ti³⁺ signal ($g \approx 1.998$) of FR-TiO₂ is higher than that of PR-20 TiO₂, which indicates FR-TiO₂ NTAs prepared by 3000 s reduction carries a higher amount of Ti³⁺ defects in the bulk of TiO₂, i.e., originating from the overall longer reduction time during electrochemical TiO₂ nanotube formation, and this also corresponds to a higher visible light absorption of the material. which indicates FR-TiO₂ NTAs prepared by 3000 s reduction carries a higher amount of Ti³⁺ defects in the bulk of the TiO₂, and this corresponds also to a higher visible light absorption of the material. In our experiments, all the tube layers after the electrochemical reduction process show a black color, but the color turns to dark gray after annealing.

The secondary but apparent resonance line at $g \approx 1.984$ can be attributed to Ti³⁺ dislocated from the regular position.^{[16],[40],[41]} Liu *et al.* and Zhou *et al.* ^{[16],[41]} found that such off-regular position Ti³⁺ defects act as intrinsic co-catalytic centers that enable photocatalytic hydrogen generation activity under open-circuit conditions. Therefore, the broad EPR signal is considered to originate from a similar type of (catalytically active) Ti³⁺ defect. Please note that for the signal at ≈ 1.984 , a higher intensity is observed for PR-20-TiO₂ NTAs, compared with FR-tubes.

X-ray photoelectron spectroscopy (XPS) spectra of Ti 2p and O 1s of PR-20 and FR-TiO₂ NTs before and after annealing are shown in **Figure S3**. These results show no detectable Ti³⁺/oxygen vacancies on the surface of any TiO₂ NTAs. This shows that within the penetration depth of XPS, the Ti³⁺ concentration is below the detection limit.

Figure 3 Photocatalytic H₂ production of different TiO₂ NTs under open circuit conditions in methanol/water (50/50 vol %) with different reduced tubes, fully reduced and non-reduced tubes under AM 1.5 (100 mW/cm²) illumination.

In order to assess the photocatalytic performance of these materials in terms of the effect of the reduction treatments (causing Ti³⁺ states and faceting), we measured photocatalytic H₂ evolution activities (**Figure 3**) of these samples obtained by various experimental conditions, including different time duration of negative voltage, reductive modes (*i.e.* unreduced, partially reduced and fully reduced). These experiments were performed under open-circuit conditions using an aqueous methanol solution (50 vol %) illuminated under AM 1.5 (100 mW/cm²) condition without the presence of any co-catalyst. The reference samples include two fully reduced tubes marked as FR-1 and FR-2 TiO₂ NTAs that have been reduced at -60 V for 3000 s and 1500 s, respectively, as well as fully reduced-bamboo tubes (denoted as NR0-R-TiO₂ NTAs) that were not exposed to reductive voltages (only returned to an non-reducing 0 mV).

It can be seen that the amorphous PR-20 TiO₂ NTAs do not have the ability to produce H₂. Annealed fully reduced tubes produce a higher amount of H₂ than non-reduced tubes. But clearly the highest H₂ production is obtained for the alternatively polarized sample denoted as PR-20-TiO₂ NTAs – here a H₂ evolution rate of 8.4 μL·h⁻¹·cm⁻² can be obtained. Please note that the NR0-TiO₂ NTAs show only a negligible H₂ production activity that is comparable to the NR-TiO₂ NTAs or fully reduced (NR0-R-TiO₂ NTAs).

Figure 4. (a) IPCE spectra of NR, PR-20 and FR TiO₂ NTAs (in 0.1 M Na₂SO₄); the inset plots are evaluation of the band gap energy of the samples from (a); (b) IMPS spectra of NR, PR-20 and FR TiO₂ NTAs (in 0.1 M Na₂SO₄); (c) V_{OC} of NR, PR-20 and FR TiO₂ NTAs in 0.1 M Na₂SO₄.

In order to further characterize the tube layers, we carried out incident photon-to-current conversion efficiency (IPCE) measurements of FR, PR-20, and NR-TiO₂ NTAs to evaluate the interplay between the photo activity and light absorption as shown in **Figure 4a**. In comparison with the reference samples, PR-20 TiO₂ NTAs exhibit the highest IPCE value in UV region and reach IPCE values as high as 50%. $(\text{IPCE} \cdot h\nu)^{0.5}$ vs. $h\nu$ plots are inserted in **Figure 4a**, from which band gap (E_g) values for an indirect transition can be evaluated. The band gap of non-reduced TiO₂ is 3.13 eV, which is in line with the characteristic value of anatase. The E_g of PR-20 and FR-TiO₂ NTAs are 3.10 and 3.06 respectively, which are slightly lower (slightly redshifted) than the NR-TiO₂ NTAs. Such a mild redshift has in literature also been reported for hydrogenated

anatase and has been ascribed to induced states close to the conduction band of anatase.
[19],[42]

Figure 4b shows the photo-generated electron transfer time constants (τ_{tr}) of FR, PR-20 and NR TiO₂ NTAs obtained from intensity modulated photocurrent spectroscopy measurements (IMPS). From the results, the τ_{tr} in the partially reduced nanotube is clearly faster than that of non-reduced nanotubes. Compared to the fully reduced nanotubes, the PR-20 TiO₂ NTAs also shows shorter transport times, which means partially reduced tubes produce the most favorable conditions for electron transport.

Electron diffusion coefficients (D_{diff}) of samples were calculated from the electron transport time constants and tube lengths as shown in **Table 2**. The D_{diff} of PR-20 TiO₂ NTAs shows the highest values under different intensity of light irradiation, with values that are two times higher than those of FR-TiO₂ NTAs.

Additionally open circuit voltage (V_{oc}) decay measurements were carried out to estimate the photo-generated electron life times of the various samples as shown in **Figure 4c**, which also shows a most beneficial effect for the bamboo-type partially reduced sample.

Mott-Schottky plots (**Figure S4**) for the different tubes show that self-doping with Ti³⁺ does not change the semiconductor type of reduced TiO₂ NTAs, *i.e.* in every case a typical n-type semiconductor characteristics is obtained. The linear parts of the curves are extrapolated to $1/C^2=0$ and the values of E_{fb} are estimated to be -0.18, -0.14 and 0.1 eV vs. Ag/AgCl for the PR-20, FR and NR TiO₂ NTAs, respectively. The negative shift of E_{fb} after the electrochemical reduction suggests a slight shift of the Fermi level due to the self-doping of Ti³⁺, in line with literature [43]. The FR-TiO₂ NTs present the most carrier density ($8.1 \times 10^{19} \text{ cm}^{-3}$), which is higher than those of PR-20-TiO₂ NTs ($3.1 \times 10^{19} \text{ cm}^{-3}$) and NR-TiO₂ NTs ($1.68 \times 10^{19} \text{ cm}^{-3}$). An increased value of N_D in semiconductors improves the charge conductivity, leading to an enhanced photocatalytic performance of the materials.

Overall we observe a remarkably high H_2 evolution rate for bamboo type, partially reduced anodic TiO_2 nanotube arrays under open circuit conditions – this without the use of any noble-metal co-catalyst. We ascribe this intrinsic activation to a synergetic effect of preferential faceting and the presence of specific Ti^{3+} species.

The formation NTAs using anodic/cathodic pulses leads to bamboo-like structures along the tube walls where (001) faceting is preferentially observed at the knots and (101) faceting in the smooth parts of tubes between the knots. It has been widely reported in literature ^[25,44,45] that the high energy (001) facets can provide an effective oxidation site while the (101) facet works as reduction site.^[25,44,45] Thus one may conclude that the (001) and (101) facets growing oriented in different parts of bamboo-like TiO_2 NTAs can facilitate the separation of photo-generated electron-hole pairs and offer a longer spatial distance to restrain the recombination of photo-generated carriers.

On the other side, the formation of the specific Ti^{3+} and V_O can provide states that mediate the transfer of electrons from the conduction band of TiO_2 to the electrolyte and enhance the electron transport within the tubes. This is suggested from the IPCE and IMPS results.

As a result we observe a higher H_2 evolution rate for pulse-reduced TiO_2 NTs in comparison with non-reduced, fully-reduced or non-bamboo type tubes.

Conclusions

In conclusion, we show an electrochemical reduction strategy to synthesize partially reduced anodic TiO_2 NTAs with bamboo-type hierarchical structure. Under solar simulator illumination, these materials exhibit enhanced H_2 evolution rate under open-circuit condition without the use of noble metal co-catalyst. The tubes produced by alternating voltages show – after rapid annealing – faceting with (001) and (101) facets exposed at knot and smooth parts of tubes, respectively. At the same time, Ti^{3+}/V_O centers are present in the reduced TiO_2 NTAs. These reduced states can mediate the transfer of electrons from TiO_2 to electrolyte.

These findings are considered to have a synergistic effect on the separation, transport and transfer of photo-generated carriers. As a result, the faceted bamboo-type self-doped TiO₂ NTAs show much faster transport rate of photo-carriers and more efficient charge separation, which is conceived to be the key reason for the enhanced photocatalytic performance of these faceted tubes.

Experimental Section

Preparation of the partially reduced knot-type structure TiO₂

The TiO₂ NTAs were grown by potentiostatic anodization of titanium foils (0.125 mm thickness, Advent, 99.6% high-purity) in an electrolyte, which consisted of 0.2 M NH₄F (98%, Sigma-Aldrich), 1 M DI water and ethylene glycol (99.5%, Sigma-Aldrich) in a two-electrode configuration using platinum as counter electrode. Before anodization, the Ti foils were sonicated in acetone, ethanol and deionized water for 15 minutes respectively, and then were dried in a nitrogen stream.

For all the TiO₂ NTAs used in our experiment the anodizing voltage was set as given in **Table 1**. For PR-20-TiO₂ NTAs for example, the parameters mean applying positive 60 V for 150 s and then switching to -20 V (negative) for 150 s as one cycle, and the whole experiment was carried out for 20 cycles. Fully reduced and non-reduced TiO₂ NTAs were prepared as references, and they were denoted as FR-TiO₂ and NR-TiO₂ NTAs, respectively. The FR-TiO₂ NTAs were prepared by applying an anodizing voltage of 60 V for 3000 s and then switching to -20 V for a certain reduction time. The NR-TiO₂ NTAs were prepared by setting the anodizing voltage to 60 V for 3000 s. The anodized samples were rinsed by ethanol directly to remove the residual electrolyte and then immersed in ethanol for half an hour.

In order to convert the amorphous tube layers to crystalline, thermal annealing was performed in air using a rapid thermal annealer (Jipelec JetFirst 100) at 500 °C for 10 s with a temperature ramp rate of 1 °C/s. As Ti sub-oxides were reported to be very

sensitive to the environmental exposure, we chose a fast and mild thermal annealing method to transform the amorphous tubes to anatase.

Table 1. Detailed description of experimental parameters of samples

Parameter setting	annotation
(60 V)-30 s- (-20 V)-30 s (100 cycles)	PR-100-TiO ₂ NTs
(60 V)-50 s- (-20 V)-50 s (60 cycles)	PR-60-TiO ₂ NTs
(60 V)-150 s- (-20 V)-150 s (20 cycles)	PR-20-TiO ₂ NTs
Amorphous (60 V)-150 s- (-20 V)-150 s (20 cycles)	A-PR-20-TiO ₂ NTs
(60 V)-300 s- (-20 V)-300 s (10 cycles)	PR-10-TiO ₂ NTs
(60 V)-3000 s- (-20 V)-3000 s	FR-1-TiO ₂ NTs
(60 V)-3000 s- (-20 V)-1500 s	FR-2-TiO ₂ NTs
(60 V)-3000 s	NR-TiO ₂ NTs
(60 V)-150 s- (0 V)-150 s (20 cycles)	NR0-TiO ₂ NTs
(60 V)-150 s- (0 V)-150 s (20 cycles)-(-20 V)-150 s	NR0-R-TiO ₂ NTs

Characterization

In order to characterize the morphology of the samples, a field-emission scanning electron microscope (SEM, Hitachi S4800) was used.

The detailed morphology including the structure of atomic lattice of PR-20-TiO₂ NTAs was observed by using high-resolution transmission electron microscopy (HRTEM, JEM 2010FEF HRTEM, JEOL, Japan).

An X-ray photoelectron spectrometer (XPS, PHI 5600 XPS spectrometer, US) was used to obtain information on the chemical binding energy of the samples. And all XPS element peaks were shifted in relation to the C1s standard position.

XRD patterns of the crystallized TiO₂ NTs were collected using an X-ray diffractometer (X'Pert Philips PMD diffractometer) equipped with a Panalytical X'celerator detector and using graphite monochromized CuK α radiation ($\lambda=1.54056$ Å).

EPR spectra were recorded on a JEOL continuous wave spectrometer JES-FA200 equipped with an X-band Gunn oscillator bridge, a cylindrical mode cavity, and a helium cryostat. The samples were measured in the solid state in an air atmosphere in quartz EPR tubes with comparable loading. Background spectra were obtained on empty tubes at the same measurement conditions. The spectra shown were measured with the following parameters: Temperature 100 K, microwave frequency 8.960 GHz, modulation width 2.0 mT, microwave power 1 mW, modulation frequency 100 kHz, and time constant 0.1 s.

Mott-Schottky measurements were performed on a Zahner IM6 (Zahner Elektrik, Kronach, Germany) work station under dark conditions in 0.1 M Na₂SO₄. A three-electrode cell with Pt as a counter electrode, the sample as a working electrode and Ag/AgCl (saturated KCl) as a reference electrode. The potential window applied was -0.1 V to 0.7 V and capacitance data were evaluated at 1Hz.

According to the Mott-schottky theory, the space charge capacitance (C_{SC}) of a semiconductor is expressed as following:^[46]

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon \epsilon_0 q N_D} \left(U - U_{fb} - \frac{k_B T}{q} \right)$$

Where C_{SC} is the space charge capacitance, U is the externally applied potential, U_{fb} is the flat band potential of the semiconductor/electrolyte junction, N_D is the donor density, ϵ_0 is the permittivity of the free charge, ϵ is the permittivity of the semiconductor electrode, q is the elementary charge, k_B is the Boltzmann's constant and T is the operation temperature.

Intensity modulated photocurrent spectroscopy (IMPS) was carried out using modulated UV light emitting diode ($\lambda=369$ nm). The modulation frequency was controlled by a frequency response analyzer (FRA, Zahner IM6, Kronach, Germany). The photocurrent or photovoltage of the cell was recorded by an electrochemical

interface (Zahner IM6), and then fed back to FRA. The light intensity incident on the cell was measured using a calibrated Si photodiode. A three-electrode cell with Pt as a counter electrode, a Haber-Luggin capillary with Ag/AgCl (saturated KCl) electrode as a reference electrode and the sample as a working electrode was used.

The open circuit voltage (V_{OC}) decay measurements were carried out by irradiating sample for 10 s and then recording the photovoltage over time.

Table 2: Diffusion coefficient of NR, PR-20 and FR NTs

Tube length L (μm)		$D_{\text{diff}} (*10^{-6} \text{ m}^2.\text{s}^{-1})$		
		1 w	10 w	50 w
NR-TiO ₂ NTs	7.44	0.21	0.21	0.21
PR-20-TiO ₂ NTs	8.41	1.79	1.53	1.53
FR-TiO ₂ NTs	11.29	0.83	0.69	0.69

* The equation is $D_{\text{diff}} = \frac{L^2}{2.35\tau_{\text{tr}}}$, where τ_{tr} is taken from **Figure 4b**.

The incident photon to current conversion efficiency (IPCE) measurements were carried out with a setup consisting of a 150 W Xe arc lamp (LOT-Oriel Instruments) as the irradiation source and a Cornerstone motorized 1/8 m monochromator. Photocurrent spectra were acquired in 0.1 M (Na₂SO₄) at a potential of 500 mV (vs. Ag/AgCl). Photocurrent spectra were measured in a three-electrode configuration, consisting of TiO₂ nanotubes as photoanode, platinum foil as a counter electrode and an Ag/AgCl electrode as a reference by a JAISSE IMP 83 PCT-BC Potentiostat-Galvanostat. The IPCE can be expressed by the following equation

$$\text{IPCE} = \frac{(1240I)}{\lambda J_{\text{light}}}$$

Where I is the measured photocurrent density at a specific wavelength, λ is the wavelength of incident light, and J_{light} is the measured irradiance power density at a specific wavelength.

Measurement of photocatalytic activity

The photocatalytic activities of the samples were evaluated by H₂ evolution measurements under open-circuit conditions without using a co-catalyst. The TiO₂ NTs (the full anodized area was calculated as 0.785 cm²) were immersed in an aqueous methanol solution (50 vol.%) and illuminated by an AM 1.5 solar simulator. A gas chromatography (GCMS-QO2010SE, SHIMADZU) with TCD detector was used to obtain the amount of H₂ generated from the different TiO₂ NTs samples.

Acknowledgements

The authors would like to acknowledge ERC, DFG and the Erlangen DFG cluster of excellence (EAM) as well as EXC315 (Bridge) for financial support. The author would also like to thank the Chinese Scholarship Council for financial support for Prof. Ji's visit to department of Materials Science, WW-4, University of Erlangen-Nuremberg.

Keywords: TiO₂ NT arrays • bamboo-type structures • cathodic reduction • hydrogen evolution

References

- [1] A. Fujishima, X. Zhang, D. A. Tryk, *Surf. Sci. Rep.* **2008**, 63, 515.
- [2] D. W. Bahnemann, M. Hilgendorff, R. Memming, *J. Phys. Chem. B* **1997**, 101, 4265.
- [3] A. Kudo, *Catal. Surv. Asia* **2003**, 7, 31.
- [4] A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobiol. C* **2000**, 1, 1.
- [5] A. Fujishima, K. Honda, *Nature* **1972**, 238, 37.
- [6] X. Chen, L. Liu, F. Huang, *Chem. Soc. Rev.* **2015**, 44, 1861.
- [7] M. Ge, C. Cao, J. Huang, S. Li, Z. Chen, K.-Q. ZHANG, S. S. Al-deyab, Y. Lai, *J. Mater. Chem. A* **2016**, 4, 6772.
- [8] L. Tian, J. Xu, A. Alnafisah, R. Wang, X. Tan, N. A. Oyler, L. Liu, X. Chen,

- Chem. Eur. J.* **2017**, 10.1002/chem.201606027.
- [9] C. Dette, M. A. Pérez-Osorio, C. S. Kley, P. Punke, C. E. Patrick, P. Jacobson, F. Giustino, S. J. Jung, K. Kern, *Nano Lett.* **2014**, 14, 6533.
 - [10] R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, *Chem. Rev.* **2014**, 114, 9824.
 - [11] X. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science* **2011**, 331, 746.
 - [12] K. Lee, R. Hahn, M. Altomare, E. Selli, P. Schmuki, *Adv. Mater.* **2013**, 25, 6133.
 - [13] K. Connelly, a. K. Wahab, H. Idriss, *Mater. Renew. Sustain. Energy* **2012**, 1, 3.
 - [14] M. Ni, M. K. H. Leung, D. Y. C. Leung, K. Sumathy, *Renew. Sustain. Energy Rev.* **2007**, 11, 401.
 - [15] N. T. Nguyen, M. Altomare, J. E. Yoo, N. Taccardi, P. Schmuki, *Adv. Energy Mater.* **2016**, 6, 1501926.
 - [16] N. Liu, C. Schneider, D. Freitag, M. Hartmann, U. Venkatesan, J. Müller, E. Spiecker, P. Schmuki, *Nano Lett.* **2014**, 14, 3309.
 - [17] N. Liu, C. Schneider, D. Freitag, U. Venkatesan, V. R. R. Marthala, M. Hartmann, B. Winter, E. Spiecker, A. Osvet, E. M. Zolnhofer, K. Meyer, T. Nakajima, X. Zhou, P. Schmuki, *Angew. Chem. Int. Ed.* **2014**, 53, 14201.
 - [18] X. Zhou, N. Liu, P. Schmuki, *ACS Catal.* **2017**, 7, 3210.
 - [19] N. Liu, X. Zhou, N. T. Nguyen, K. Peters, F. Zoller, I. Hwang, C. Schneider, M. E. Miehlich, D. Freitag, K. Meyer, D. Fattakhova-Rohlfing, P. Schmuki, *ChemSusChem* **2017**, 10, 62.
 - [20] N. Liu, H.-G. Steinrück, A. Osvet, Y. Yang, P. Schmuki, *Appl. Phys. Lett.* **2017**, 110, 72102.
 - [21] N. Liu, V. Haeublein, X. Zhou, U. Venkatesan, M. Hartmann, M. MacKovic, T. Nakajima, E. Spiecker, A. Osvet, L. Frey, P. Schmuki, *Nano Lett.* **2015**, 15, 6815.
 - [22] C. Burda, X. Chen, R. Narayanan, M. A. El-sayed, *Chem. R* **2005**, 105, 1025.
 - [23] A. Tsujiko, T. Kisumi, Y. Magari, K. Murakoshi, Y. Nakato, *J. Phys. Chem. B* **2000**, 2, 4873.
 - [24] T. Tachikawa, S. Yamashita, T. Majima, *J. Am. Chem. Soc.* **2011**, 133, 7197.
 - [25] T. Ohno, K. Sarukawa, M. Matsumura, *New J. Chem.* **2002**, 26, 1167.

- [26] J. L. Giocondi, G. S. Rohrer, *Top. Catal.* **2008**, *49*, 18.
- [27] N. Liu, H.-G. Steinrück, A. Osvet, Y. Yang, P. Schmuki, *Applied Physics Letters* **2017**, *110*, 72102.
- [28] P. Roy, S. Berger, P. Schmuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 2904.
- [29] D. Kim, A. Ghicov, S. P. Albu, P. Schmuki, *Journal of the American Chemical Society* **2008**, 16454.
- [30] A. Ghicov, H. Tsuchiya, R. Hahn, J. M. MacAk, A. G. Munoz, P. Schmuki, *Electrochemistry Communications* **2006**, *8*, 528.
- [31] J. M. Macak, B. G. Gong, M. Hueppe, P. Schmuki, *Adv. Mater.* **2007**, *19*, 3027.
- [32] N. Liu, C. Schneider, D. Freitag, E. M. Zolnhofer, K. Meyer, *Chem. Eur. J.* **2016**, *22*, 13810.
- [33] J. Prochazka, L. Kavan, M. Zukalova, O. Frank, M. Kalbac, A. Zukal, M. Klementova, D. Carbone, M. Graetzel, *Chem. Mater.* **2009**, *21*, 1457.
- [34] H. G. Agrell, G. Boschloo, A. Hagfeldt, *J. Phys. Chem. B* **2004**, *108*, 12388.
- [35] A. Ghicov, S. P. Albu, J. M. Macak, P. Schmuki, *Small* **2008**, *4*, 1063.
- [36] M. Kitao, Y. Oshima, K. Urabe, *Jpn. J. Appl. Phys.* **1997**, *36*, 4423.
- [37] S. P. Albu, D. Kim, P. Schmuki, *Angewandte Chemie - International Edition* **2008**, *47*, 1916.
- [38] F. Zuo, L. Wang, T. Wu, Z. Zhang, D. Borchardt, P. Feng, *Journal of the American Chemical Society* **2010**, *132*, 11856.
- [39] J. Chen, G. Wu, T. Wang, X. Li, M. Li, Y. Sang, H. Liu, *ACS Applied Materials and Interfaces* **2017**, *9*, 4634.
- [40] S. Mohajernia, S. Hejazi, A. Mazare, N. T. Nguyen, P. Schmuki, *Chemistry - A European Journal* **2017**, *23*, 12406.
- [41] X. Zhou, N. Liu, J. Schmidt, A. Kahnt, A. Osvet, S. Romeis, E. M. Zolnhofer, V. R. R. Marthala, D. M. Guldi, W. Peukert, M. Hartmann, K. Meyer, P. Schmuki, *Adv. Mater.* **2017**, *29*, 1604747.
- [42] X. Zhou, V. Häublein, N. Liu, N. T. Nguyen, E. M. Zolnhofer, H. Tsuchiya, M. S. Killian, K. Meyer, L. Frey, P. Schmuki, *Angew. Chem. Int. Ed.* **2016**, *55*, 3763.

- [43] P. Deák, J. Kullgren, B. Aradi, T. Frauenheim, L. Kavan, *Electrochim. Acta* **2016**, *199*, 27.
- [44] M. Liu, L. Piao, L. Zhao, S. Ju, Z. Yan, T. He, C. Zhou, W. Wang, *Chem. Commun.* **2010**, *46*, 1664.
- [45] S. Selcuk, A. Selloni, *Nature Materials* **2016**, *15*, 1107.
- [46] H. Tsuchiya, J. M. Macak, A. Ghicov, A. S. Räder, L. Taveira, P. Schmuki, *Corros. Sci.* **2007**, *49*, 203.