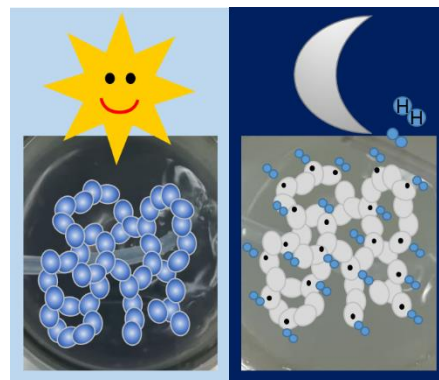


# Photocatalytic hydrogen generation and electron storage capability of mesoporous TiO<sub>2</sub> aerogels with adjustable surface area

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**Abstract.** Mesoporous TiO<sub>2</sub> aerogels with surface area larger than 600 m<sup>2</sup> g<sup>-1</sup> have been prepared *via* acid-catalyzed sol-gel synthesis and supercritical drying. Varying temperature treatment in air results in changes in the morphology of the aerogels and their specific surface area. Increasing the calcination temperature to 500 °C results in decreased surface area, however in strongly increased hydrogen evolution rates in photocatalytic experiments. Moreover, electron storage capabilities of different TiO<sub>2</sub> aerogels are investigated. The ability to store photogenerated electrons in the surface states of the aerogels upon illumination of dispersions in water-methanol mixtures increases with lower calcination temperature. Furthermore, the extent of electron storage also depends on hole scavenger concentration. Finally, nitrogen reduction to ammonia in the dark is performed with photogenerated stored electrons in TiO<sub>2</sub> aerogels, separating the charge carrier photogeneration from the dark reduction reaction.



**Keywords:** TiO<sub>2</sub> aerogel, Electron storage, Photocatalysis, Hydrogen production, Nitrogen reduction

## 1. Introduction

Aerogels are unique 3D mesoporous materials of interconnected porous networks which exhibit high surface areas, open pores and low densities.<sup>[1,2]</sup> The sol-gel process is a prominent technique to synthesize such aerogels, since it is a simple method and requires no complex setup. Several synthesis parameters can be varied to control the nanoscale structure and physicochemical properties.<sup>[3,4]</sup> It has been demonstrated that high surface areas could be obtained in amorphous titania aerogels based on chloride and alkoxide precursors followed by hydrolysis and condensation reaction forming a wet gel<sup>[5,6]</sup> which is further dried e.g. supercritically to prevent the porous

structure to collapse.<sup>[1]</sup> The ability to control the sol-gel process for synthesizing aerogels is a powerful tool for designing a suitable and efficient catalyst. A high specific surface area and open porosity of aerogels favors the adsorption and diffusion of reactants, therefore offers many active reaction sites and their accessibility for photocatalytic reactions.<sup>[7]</sup>

The interconnected network of nanoparticles offers additionally long diffusion pathways for photogenerated electrons. With intensity-modulated photovoltage spectroscopy and photocurrent spectroscopy measurements on TiO<sub>2</sub> aerogels, synthesized with different weight fractions of sol-gel precursors, DeSario *et al.* were able to show that

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trapping sites are the reactive sites in photocatalytic hydrogen generation.<sup>[8]</sup> This could be concluded due to differences in lifetime and mobility of photogenerated electrons. Hydrogen generation increased with increased sol-gel precursor concentration. By use of UV-Vis and EPR spectroscopy, Di Iorio *et al.* found an improved electron storage capacity for TiO<sub>2</sub> ethanolic sols with an increase of titanium to water molar ratio.<sup>[9]</sup> Panayotov *et al.* reported that photogenerated electron-hole pairs in TiO<sub>2</sub> aerogels are more efficiently separated compared to commercial TiO<sub>2</sub> nanoparticles and that the density of excited-state electrons is higher in these aerogels.<sup>[10]</sup>

Besides the discussed aerogel structure, the crystal structure also has an influence on the charge carrier lifetime. Sachs *et al.* performed transient absorption spectroscopy measurements on the most commonly used TiO<sub>2</sub> crystals phases, i.e. rutile and anatase. They found a faster recombination rate for the rutile crystal phase and that for both polymorphs, the surface recombination is the most important factor for the charge carrier lifetime.<sup>[11]</sup>

There are several examples in the literature which report the storage of photoexcited electrons in semiconductor materials, and the use of these stored electrons for reduction reactions. Bahnemann *et al.* reported the trapping of electrons close to the surface of colloidal TiO<sub>2</sub> with the formation of Ti<sup>3+</sup> states in presence of a hole scavenger, which was characterized by a broad absorption with a maximum at 650 nm.<sup>[12]</sup> They performed further investigation on the electron storage of TiO<sub>2</sub>. By employing the stopped flow technique and UV-Vis spectroscopy, they investigated the reduction reaction of the stored electrons with silver ions<sup>[13]</sup>, gold ions<sup>[14]</sup>, and other electron acceptors in detail.<sup>[15,16]</sup> In 2011, they showed for the first time that photoexcited electrons stored in TiO<sub>2</sub> can reduce nitrogen.<sup>[17]</sup> Since then, reports about the electron storage of different materials<sup>[18]</sup> including WO<sub>3</sub>,<sup>[19]</sup> copper complexes,<sup>[20]</sup> and carbon nitrides<sup>[21]</sup> were published. In case of cyanamide-functionalized polymeric networks of heptazine units, 4-methylbenzyl alcohol was necessary as hole acceptor to store electrons in the material. In contrast to this, an aqueous methanol solution with a concentration of 0.02 mol L<sup>-1</sup> is already enough to extract photoexcited holes and to store photoexcited electrons in TiO<sub>2</sub>.<sup>[17]</sup> The addition of a co-catalyst like Pt or other metal co-catalysts to a photocatalyst storing photoexcited electrons in aqueous solution, lead to the formation of hydrogen.<sup>[13,14,21,22]</sup>

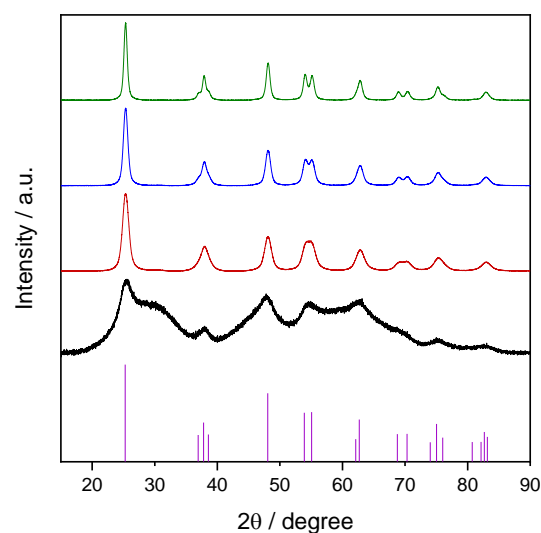
In the present work, we report a detailed investigation on the photocatalytic and electron storage properties of mesoporous TiO<sub>2</sub> aerogels prepared *via* an acid catalyzed sol-gel method with subsequent supercritical

drying and different heat treatments in air. All prepared TiO<sub>2</sub> aerogels exhibit the anatase crystal structure to exclude the influence of a composite formation on the photocatalytic activity and electron storage ability of the aerogels. The influence of the physical properties, especially the surface area and crystallinity, on the ability to store electrons in water-methanol slurry and on hydrogen evolution are discussed in detail. Methanol concentration-dependent measurements on samples with high electron storage ability are presented furthermore, and an experiment for nitrogen reduction in the dark yielding ammonia, using such stored electrons as a possible ammonia-on-demand application for the herein synthesized aerogels.

## 2. Results and Discussion

### 2.1 Sample Characterization

X-ray diffraction (XRD) patterns of the as-synthesized and calcined TiO<sub>2</sub> aerogels are shown in **Figure 1**. It can be observed that surprisingly the as-synthesized TiO<sub>2</sub> aerogel (please see Experimental Section for details) is semi-crystalline. The broad diffraction peaks represent a high amorphous content, but the main reflections at 25.28° and 48.05° 2 $\theta$  agree with the main reflections of anatase TiO<sub>2</sub> (PDF-21-1272). Typically, supercritically-dried aerogels are reported to be amorphous using similar synthesis conditions.<sup>[5,6]</sup>



**Figure 1.** XRD patterns of the as-synthesized TiO<sub>2</sub> aerogel (black) and aerogels calcined at 300 °C (red), 400 °C (blue) and 500 °C (green). Reference line pattern of anatase TiO<sub>2</sub> (PDF-21-1272) is shown for comparison. Normalized data to the range 0 to 100 related to the highest signal.

The heat-treated TiO<sub>2</sub> aerogels at 300°C, 400°C and 500°C show reflections which can be assigned to the TiO<sub>2</sub> anatase crystal structure. Furthermore, no

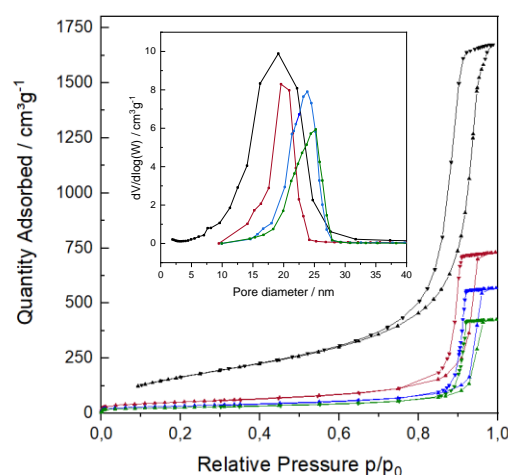
reflections can be assigned to TiO<sub>2</sub> rutile crystal structure. According to literature, anatase is the most likely occurring crystal structure at the applied calcination temperatures.<sup>[6]</sup> The anatase-rutile phase transition was reported to occur at temperatures between 400-800 °C.<sup>[3]</sup> The XRD pattern of the calcined aerogel at 500 °C exhibits well-defined and better resolved reflections compared to the calcined aerogels at 300 °C and 400 °C, respectively. This indicates that the crystallinity increases with the calcination temperature. The crystallite sizes of the aerogels were estimated for (101) preferred oriented anatase TiO<sub>2</sub> in the range of 23°-28° 2 $\theta$ . They increase with calcination temperature from 3.8 nm for the as-synthesized TiO<sub>2</sub> aerogel to 12.9 nm for TiO<sub>2</sub> aerogel calcined at 500 °C (**Table 1**).

The adsorption and desorption isotherms of the as-synthesized and heat-treated TiO<sub>2</sub> aerogels are presented in **Figure 2**. They exhibit a type IVa isotherm with H1 hysteresis loop according to the IUPAC classifications indicating a mesoporous material.<sup>[23]</sup> The desorption path is in thermodynamic equilibrium and different to the adsorption path, leading to hysteresis which is associated with delayed capillary condensation during adsorption.<sup>[24,25]</sup> The type H1 hysteresis loop and the steep adsorption branch indicate a uniform and narrow pore size distribution. The adsorbed volume of nitrogen increases strongly at a relative pressure of  $p/p^0=0.6$  for the as-synthesized TiO<sub>2</sub> aerogel before it reaches a plateau, indicating capillary condensation and saturation. For the heat-treated TiO<sub>2</sub> aerogels the steep adsorption branch occurs at higher relative pressures, in particular the higher the calcination temperature the higher the relative pressure for the increase of adsorbed volume. This indicates larger pores after higher calcination temperatures. This is in good agreement with the pore size distribution shown in **Figure 2 (inset)**.

A narrow pore size distribution was obtained for the as-synthesized and heat-treated TiO<sub>2</sub> aerogels, whereby the pore size distribution is slightly narrower and the BJH-derived average pore size shifts to larger pore sizes for the heat-treated samples. This is in good agreement with the location of hysteresis loops, which occur at higher relative pressure and in a narrower pressure range for higher calcination temperatures. This can be explained by smaller mesopores (approx. 5-15 nm) which coalesced with larger mesopores (approx. 20 nm). The reduced number of smaller mesopores could also explain the decreased surface area after heat-treatment, as smaller pores contribute more to higher surface areas.<sup>[6]</sup>

The physisorption results are summarized in **Table 1**. It shows the effect of calcination temperature on the

specific surface area and cumulative pore volume. The as-synthesized TiO<sub>2</sub> aerogel exhibits high specific surface area and pore volume of 642 m<sup>2</sup>/g and 2.59 cm<sup>3</sup>/g, respectively. The supercritical drying process preserves the mesoporous structure of the as-synthesized TiO<sub>2</sub> aerogel leading to the observed high values. Similar results have been reported in literature by Sadriyeh *et al.*, however the aging time could be reduced from >40 days to 7 days during synthesis here, achieving a stable and translucent TiO<sub>2</sub> aerogel.<sup>[6]</sup> As expected, the surface area as well as the pore volume decrease for the heat-treated TiO<sub>2</sub> aerogel at 300 °C. The surface area and pore volume show a further decrease for the TiO<sub>2</sub> aerogels heat-treated at 400 °C and 500 °C, indicating a decrease in porosity. This is in accordance with the results reported in literature for calcined aerogel samples.<sup>[6]</sup> Even though the calcination of the TiO<sub>2</sub> aerogel reduced the specific surface area and porosity, both are higher compared to conventional bulk anatase, and therefore it is beneficial using the investigated sol-gel synthesis conditions and supercritical drying for TiO<sub>2</sub> aerogel synthesis.<sup>[6]</sup>



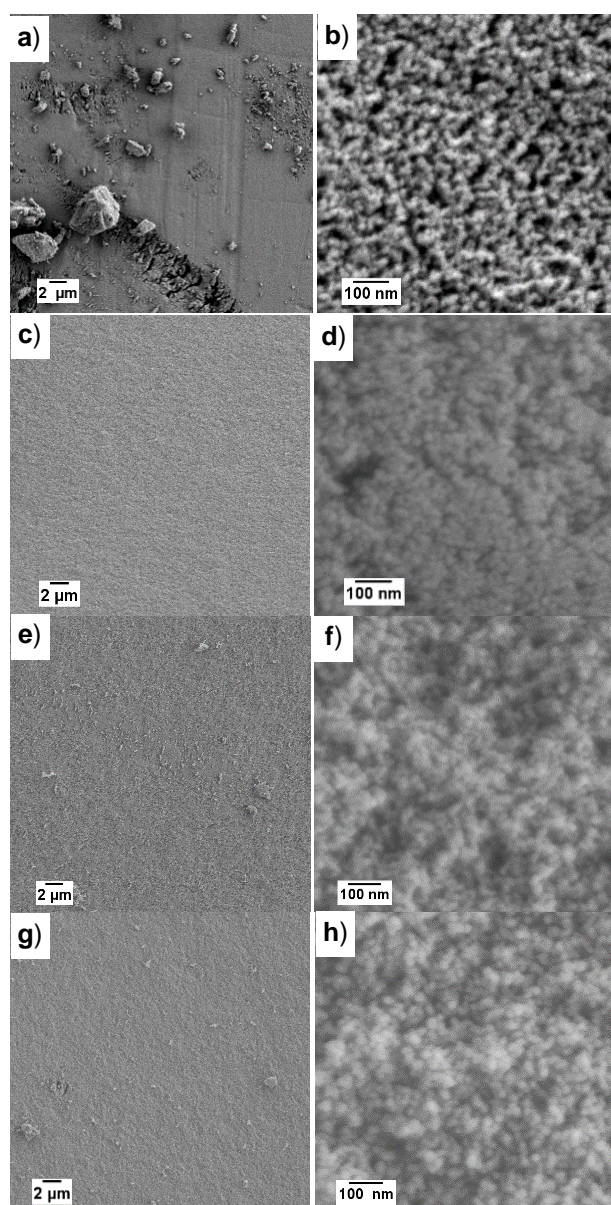
**Figure 2.** N<sub>2</sub> physisorption isotherms and BJH pore size distribution (inset) for the as-synthesized and heat-treated TiO<sub>2</sub> aerogels; as-synthesized TiO<sub>2</sub> aerogel (black) and aerogels calcined at 300 °C (red), 400 °C (blue) and 500 °C (green).

**Table 1.** Nitrogen physisorption results, crystallite sizes, and band gaps of the prepared TiO<sub>2</sub> aerogel samples.

	BET surface area / m <sup>2</sup> g <sup>-1</sup>	Cumulative pore volume / cm <sup>3</sup> g <sup>-1</sup>	Average pore diameter / nm	Crystallite size / nm	Band gap/ eV
as-synthesized	642	2.59	19	4(3.8)	3.5
300 °C	184	1.13	20	7(6.9)	3.3
400 °C	118	0.88	24	10(9.5)	3.3
500 °C	92	0.66	25	14(12.9)	3.2

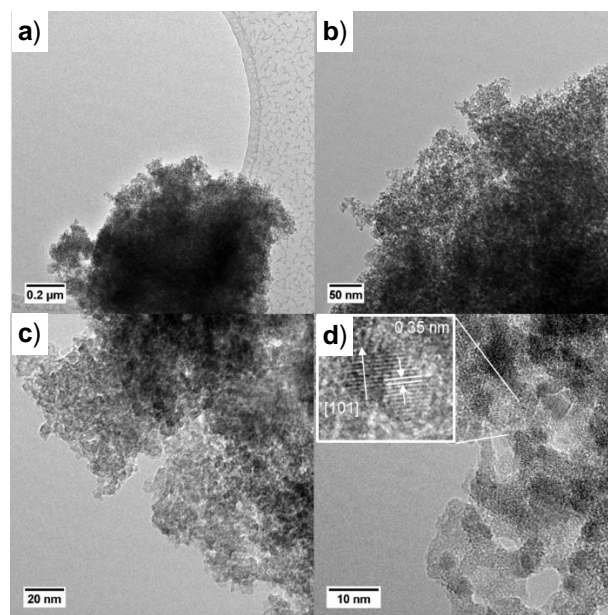


**Figure 3** shows the SEM images of the different TiO<sub>2</sub> aerogels at two different magnifications. The as-synthesized samples show mainly a smooth surface, apart from smaller cracks and fragments. The high magnification SEM image shows small, nearly spherical interconnected particles which form an open porous network. **Figure 3 c-h** show the SEM images of the heat-treated TiO<sub>2</sub> aerogels at 300 °C, 400 °C and 500 °C. The images show also a smooth uniform surface of the samples, however the porosity of the samples decreases with higher calcination temperature, which is visible through the few voids between the particles and denser appearance of the microstructure. The particles become larger with higher calcination temperature and seem to be arranged more densely. This is in good agreement with the N<sub>2</sub> physisorption results in **Figure 2** and **Table 1**.



**Figure 3.** SEM images of the a-b) as-synthesized aerogel, c-d) calcined aerogel at 300 °C, e-f) calcined aerogel at 400 °C, g-h) calcined aerogel at 500 °C, at lower (5.000x) and higher (200.000x) magnification.

The as-synthesized TiO<sub>2</sub> aerogel was further analyzed using TEM, to confirm the observed semi-crystalline structure. **Figure 4** shows the TEM images of the as-synthesized TiO<sub>2</sub> aerogel at different magnifications. Amorphous particles and nanocrystals can be observed. This is in good agreement with the XRD results shown in **Figure 1**, where a semi-crystalline structure was assumed. The TEM image shows the interconnected particles and nanocrystals in the porous network. It can be assumed that the particles in the aerogel network are connected by chemical means, rather than physical connection as in P25 nanopowder. This is advantageous for photocatalytic hydrogen evolution, as this could improve the separation of charge carriers. It was reported that the interconnected structure of TiO<sub>2</sub> nanocrystals offers better charge carrier delocalization compared to TiO<sub>2</sub> nanoparticle aggregates, e.g. P25 which are physically connected.<sup>[26,27]</sup> The inset in **Figure 4** shows the d-spacing which was estimated 0.35 nm for the observed nanocrystals. This fits to the (101)-oriented anatase TiO<sub>2</sub> phase and confirms the semi-crystalline nature of the as-synthesized TiO<sub>2</sub> aerogel. The size of the nanocrystals was estimated approx. 4-6 nm, which is slightly larger compared to the calculated grain size from XRD pattern (approx. 4 nm).



**Figure 4.** TEM images of as-synthesized TiO<sub>2</sub> aerogel, a) 12.000x, b) 39.000x, c) 115.000x, d) 295.000x, the inset is a local enlargement of TiO<sub>2</sub> nanocrystal.

Absorption spectra in diffuse reflectance were recorded to characterize the optical properties of the TiO<sub>2</sub> aerogels. Diffuse reflectance spectra was converted to Kubelka-Munk spectra and Tauc plots for band gap estimation (**Figure S1**). **Table 1** summarizes the estimated band gaps of the aerogel samples. The bandgap of the untreated TiO<sub>2</sub> aerogel is with 3.5 eV

slightly higher than the bandgap of the calcined aerogels with 3.2 to 3.3 eV, which was expected as it is a partially amorphous sample. For all aerogels, only one sharp absorption edge at 340 to 375 nm is visible in the UV-vis spectra, indicating that no by-phases, like rutile are formed. The estimated bandgaps are in correspondence with the reported literature values for anatase TiO<sub>2</sub> with 3.2 eV.<sup>[26,28]</sup>

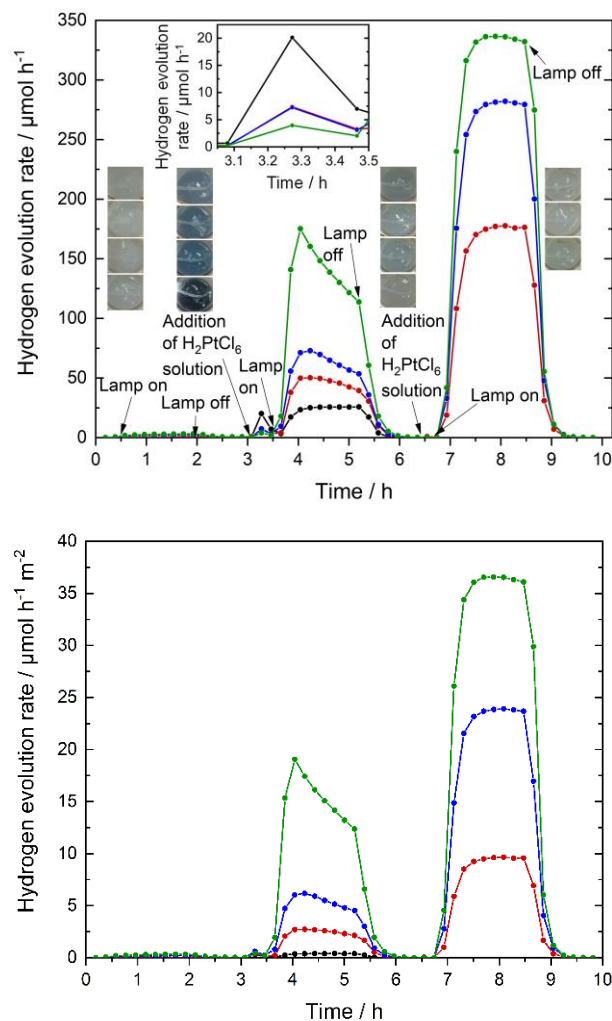
## 2.2 Photocatalytic hydrogen evolution and electron storage

Photocatalytic hydrogen evolution experiments were performed with all TiO<sub>2</sub> aerogel samples to investigate the influence of the physicochemical properties of the aerogels on photocatalytic activity (**Figure 5**). For this, 100 mg aerogel were dispersed in 150 mL of a 2.5 mol L<sup>-1</sup> aqueous methanol solution and were irradiated with a 300 W Xe solar simulator (see *Experimental Section*). The samples were first irradiated for 100 minutes without a co-catalyst. The color change of the dispersions is shown in the left graph (**Figure 5** top) going from a colorless dispersion to a blueish colored dispersion after irradiation. Enlarged versions of the photographs are given additionally in the *Supporting information* (**Figure S2** SI). This blue coloration is an indication of the storage of electrons and formation of Ti<sup>3+</sup> states.<sup>[13,15,17,29]</sup> The intensity of the blue color decreases with increasing calcination temperature of the aerogels, and therefore also with the surface area and the crystallinity of the TiO<sub>2</sub> aerogel samples. Moreover, the amounts of detected hydrogen are very low (below 10  $\mu\text{mol h}^{-1}$ ), as expected for unmodified TiO<sub>2</sub>.

After the sun simulator was switched off and the hydrogen evolution went to zero, an aqueous H<sub>2</sub>PtCl<sub>6</sub> solution was added to the blueish dispersions *via* rubber sealing (to keep the inert atmosphere), to reach an amount of 0.0076  $\mu\text{mol m}^{-2}$  Pt *via* subsequent photodeposition. However, even before continuing the light irradiation but few seconds after the addition of the co-catalyst precursor solution, the coloration of the dispersion disappeared. At the same time, a sharp peak in the hydrogen evolution rate was detected in all four cases. The intensity of this hydrogen evolution peak without light irradiation (inset **Figure 5** top) has the same trend as the intensity of the blueish color of the dispersion, the darker the dispersion before H<sub>2</sub>PtCl<sub>6</sub> addition the higher the hydrogen evolution peak after its addition.

This hydrogen evolution peak can be explained by the photogenerated and stored electrons in the aerogel sample being used to form metallic Pt clusters on the TiO<sub>2</sub> aerogels upon H<sub>2</sub>PtCl<sub>6</sub> reduction. After all Pt ions are reduced and formed Pt metal nanoparticles, a Schottky contact is formed between Pt and TiO<sub>2</sub>, upon

which the excess stored electrons in the aerogels are transferred to the Pt metal particles, where they are used to reduce protons to hydrogen acting as co-catalysts. This is then detected as the sharp peak in the hydrogen evolution curve.



**Figure 5.** Non-normalized (top) and on absolute surface area normalized (bottom) hydrogen evolution rates over time of the as-synthesized (black) and calcined TiO<sub>2</sub> aerogels, 300 °C (red), 400 °C (blue), 500 °C (green); Measured without co-catalyst for the first 100 min; measured with 0.0076  $\mu\text{mol m}^{-2}$  Pt as co-catalyst ( $\approx$  0.1 wt.-% for the as-synthesized sample) in the second 100 min, measured with 0.1 wt.-% Pt on the calcined aerogels in the third 100 min. The photographs show the dispersions before irradiation, after the first 100 min, after the second 100 min, and after the third 100 min irradiation with 500 °C, 400 °C, 300 °C and as-synthesized sample from top to bottom. Inset graph shows enlargement of the hydrogen peak after the first addition of H<sub>2</sub>PtCl<sub>6</sub> solution.

This kind of mechanism was already reported before for different metal co-catalyst deposition on TiO<sub>2</sub>.<sup>[13,14,29,30]</sup> The intensity of this peak is therefore - beneath the intensity of the blue color - an indication for the amount of stored electrons. Furube *et al.* reported an improved charge carrier separation by Pt deposition on TiO<sub>2</sub> by

use of transient absorption spectroscopy, which additionally explains the enhancement of the hydrogen evolution rate.<sup>[31]</sup>

The electron storage capability of the aerogels can be related to their physicochemical properties. The as-synthesized partially amorphous sample with the highest surface area can store the most electrons indicated by the most intense blue coloration. Ikeda *et al.* reported that electrons are trapped at defective sites in TiO<sub>2</sub> e.g. oxygen vacancies, which are mainly located at the surface of TiO<sub>2</sub>. They state that the quantity of accumulated electrons represents the number of defective sites.<sup>[32]</sup> The as-synthesized aerogel can therefore store the most photocharged electrons due to the highest surface area and presumably highest amount of surface defects, due to its low crystallinity.

An increase in the crystallinity and decrease in surface area results in a decreased amount of stored electrons. At the same time, the hydrogen evolution rates of the samples without co-catalyst follows the opposite trend of the coloration intensity, as can be seen in **Figure 6**.

The crystallinity of the aerogel has the strongest influence on the electron storage ability and the hydrogen evolution activity. The surface area and presumably number of active sites for the hydrogen evolution reaction is not the critical factor for the hydrogen evolution rate: Although the as-synthesized semi-crystalline sample offers the highest surface area and presumably highest number of active sites, it does not show the highest rate in the photocatalytic hydrogen evolution (**Figure 5**). Indeed, the sample with the smallest surface area - calcined at 500 °C - offers the best hydrogen evolution rate, which clearly shows that the crystallinity and not the surface area is the most important factor. It can be assumed that the interconnection of the TiO<sub>2</sub> nanocrystals in the aerogels improves with higher calcination temperature, which is an advantage for the photocatalytic hydrogen production, as the charge carrier separation seems to be improved as already discussed before. The heat-treatment can also reduce the amount of bulk defects, which are recombination centers. Kong *et al.* reported a reduced bulk to surface defect ratio and increased photocatalytic activity for TiO<sub>2</sub> nanocrystals, which were calcined compared to TiO<sub>2</sub> nanocrystals, which were prepared without a calcination step.<sup>[33]</sup>

In case of the semi-crystalline as-synthesized TiO<sub>2</sub> aerogel, more electrons are stored in the material and are not used for the hydrogen evolution. This is an indication that the electrons are trapped in surface defects and not in bulk defects, where electrons would recombine with holes. Surface defects are on the one hand charge carrier traps and on the other hand adsorption sites for methanol as hole scavenger.<sup>[33]</sup>

Electrons are trapped, but recombination is prevented by the fast and efficient reaction of the holes with methanol, which makes the untreated aerogel the best electron storage material in this study. Heat-treatment seems to reduce the amount of surface defects and bulk defects leading to reduced electron storage, but improved charge carrier separation and hydrogen evolution.

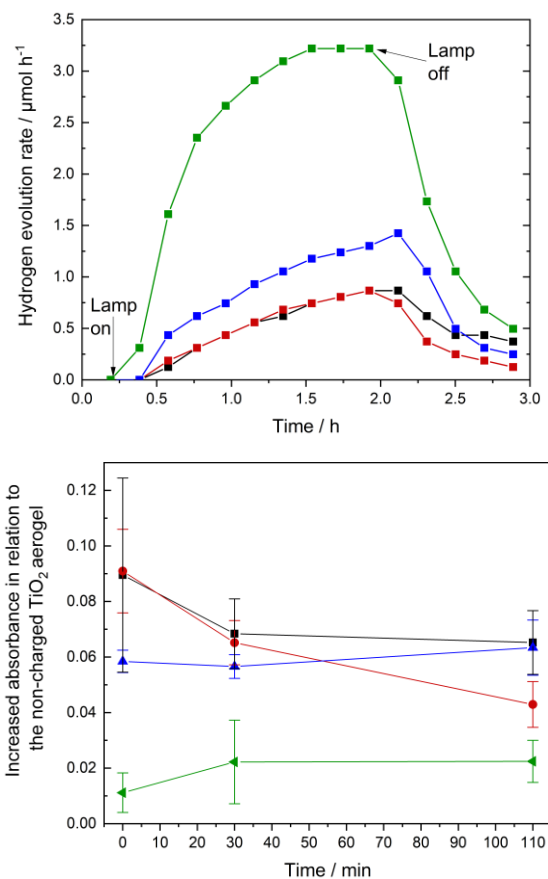
Moreover, hydrogen evolution curves in **Figure 5** show also the activity for the hydrogen evolution reaction after addition of Pt as co-catalyst. The dependence on the crystallinity of the aerogel can be seen also in this step of the photocatalytic reaction. After the deposition of the co-catalyst, no blue coloration of the dispersion can be observed anymore, as the electrons are transferred to the formed metallic Pt particles where they are used for the hydrogen evolution and not stored in the material. All samples exhibit the same amount of co-catalyst per surface area, nevertheless a clear difference in the activity is observed. As the Pt particles prevent the storage of the electrons in surface defect states, the difference in the activity can be explained by the crystallinity and the amount of bulk defects. The heat-treated aerogels with increased crystallinity show a decreased charge carrier recombination and therefore higher activity compared to the semi-crystalline aerogel. This can be explained by the decreased number of surface and bulk defects due to the calcination process as well as the photocatalytic activity of exposed facets of the crystalline phase.<sup>[34]</sup> The photocatalytic activity is also improved by the sintered and chemically linked TiO<sub>2</sub> nanoparticles, due to the wide distribution and therefore better separation of charge carriers.<sup>[35]</sup>

The deposition in wt.-% in the last step shows nicely the importance to deposit co-catalysts in dependence to the surface area of the photocatalyst. The amount of co-catalyst per m<sup>2</sup> is much higher for the calcined sample when the co-catalyst is deposited in wt.-%, which leads to a much higher Pt density on the surface than the deposition per m<sup>2</sup>. In the bottom part of **Figure 5**, the hydrogen evolution rate is therefore normalized on the absolute surface area of the aerogels in the reactor to exclude the influence of the very different surface areas of the aerogels sample, and presumably different amount of active sites. The trend in the rates stays the same, the sample with the highest surface area exhibit the highest activity. The activity of the as-synthesized sample per surface area is much lower in comparison to the calcined sample compared to the measurement not normalized to surface area. This also shows that a normalization to surface area is important for a correct interpretation of the photocatalytic activity of photocatalysts, which was already shown before.<sup>[29,36–38]</sup>



The TiO<sub>2</sub> aerogels were all regained after the photocatalytic hydrogen experiments by washing and supercritical drying. XRD pattern after the photocatalytic hydrogen production experiments are shown in **Figure S3**. The XRD pattern of the heat treated aerogels show no changes, the small amounts of Pt added are not visible. Interestingly, the as-synthesized aerogel sample exhibits a higher crystallinity than before the experiments, but offers still a semi-crystalline character. This will be investigated in future studies.

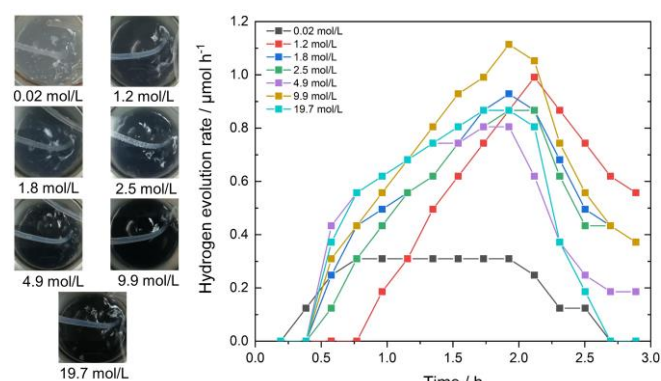
To verify the differences in the amount of stored electrons in the aerogel samples, the absorbance of the aerogel dispersions was measured in a range of 350 nm to 800 nm before and after irradiation. To detect the time-dependent change in the absorbance additionally, the absorbance was determined directly after the irradiation for 100 min, 30 min after irradiation, and 110 min after the irradiation (**Figure S4**). For this test, dispersions of 100 mg of the TiO<sub>2</sub> aerogel in 150 mL of a 2.5 mol L<sup>-1</sup> aqueous methanol solution were irradiated. The increase in absorption of the dispersions after the irradiation for 100 min was detected at a wavelength of 600 nm and compared to the absorbance of the dispersion before irradiation (**Figure 6** bottom), while additionally the hydrogen evolution was detected (**Figure 6** top). The absorbance increase directly after irradiation for 100 min is most prominent in the as-synthesized aerogel and the aerogel calcined at 300 °C, and being lower for higher calcination temperatures and therefore the crystallinity of the aerogel. This is in good agreement to the photographs taken during the hydrogen evolution reactions. A decay in absorbance increase after irradiation is most prominent for the sample calcined at 300 °C, and also detectable in the as-synthesized aerogel. For higher calcined samples, hardly any decay of the absorption increase is detectable in the investigated time range. The decay in the absorbance increase is attributable with a decreasing amount of stored electrons in the aerogel sample, which can be due to charge carrier recombination or either reduction reaction. The hydrogen evolution rates are trending in reverse to the absorbance increases of the TiO<sub>2</sub> aerogels, the highest calcined sample exhibiting the highest activity for photocatalytic hydrogen evolution. Electron storage is preferred in aerogel samples with lower crystallinity, which goes directly in line with reduced rates for photocatalytic hydrogen evolution, in accordance with the photocatalysis results.



**Figure 6.** Hydrogen evolution curves of TiO<sub>2</sub> aerogel dispersions without co-catalyst of as-synthesized (black) and calcined TiO<sub>2</sub> aerogels, 300 °C (red), 400 °C (blue), 500 °C (green) (top). The increase in absorbance at 600 nm after 100 min irradiation (time = 0 min) is given below, followed by two additional measurements (30 min or 110 min after irradiation, respectively) without irradiation indicating color fading (bottom).

Since the results of the hydrogen evolution experiments lead to the conclusion that the as-synthesized aerogel seems to offer the best electron storage ability, further experiments were performed with this sample. The influence of electron storage ability on the methanol concentration was additionally tested. Dispersions of 100 mg of the aerogel in 150 mL aqueous solution with different methanol concentrations ranging from 0.02 mol L<sup>-1</sup> up to 19.7 mol L<sup>-1</sup> were irradiated for 100 min while simultaneously hydrogen evolution was detected. Additionally, photographs of the dispersions were taken directly after the irradiation (**Figure 7**), enlarge versions of the photograph are given in the *Supporting Information* (**Figure S5**). All dispersions show the typical blue coloration as indication of the storage of electrons and formation of Ti<sup>3+</sup> states. Only a very slight coloration and presumably small amount of stored electrons are visible for the lowest methanol concentration of 0.02 mol L<sup>-1</sup> after irradiation for 100 min. This goes in line with a negligible amount of

evolved hydrogen. For all other methanol concentrations higher than 0.02 mol L<sup>-1</sup>, a comparable hydrogen evolution rate between 0.8 and 1.1  $\mu\text{mol h}^{-1}$  is detected. The higher the methanol concentration, the darker is the coloration of the dispersion after the same time of irradiation. Thus, the amount of stored electrons can be adjusted by the used methanol concentration. The higher the concentration of the hole scavenger is, the higher the amount of stored electrons, with hardly any changes in hydrogen evolution rates. From these results, it can be assumed that in case of very small amount of hole scavenger, the recombination rate at the surface defects is increased as the holes cannot react with methanol before recombining with trapped electrons. The higher the concentration of the hole scavenger, the more methanol can adsorb on surface defects and the charge carrier recombination is strongly reduced, which is visible in an increased coloration of the dispersion – an increased number of stored electrons and therefore Ti<sup>3+</sup> states in the sample. This further supports the results from the hydrogen evolution experiments. These results pave the way for future hydrogen-on-demand application, when charging and hydrogen evolution can be spatially and timely separated.



**Figure 7.** Hydrogen evolution rates over time of the as-synthesized TiO<sub>2</sub> aerogel dispersed in aqueous methanol solutions with different methanol concentrations, plus photographs of the dispersions after an irradiation time of 100 min. Irradiation was stopped after 100 min.

A material like the here presented as-synthesized TiO<sub>2</sub> aerogel with high electron storage ability and high amount of surface defects offers the possibility to apply it for other reactions, for example in dark reduction reactions of very stable molecules. One of the currently most investigated reactions of this type is for example the nitrogen reduction reaction.<sup>[39,40]</sup> Surface oxygen vacancies can be beneficial for the N<sub>2</sub> adsorption and conversion, which makes the as-synthesized TiO<sub>2</sub> aerogel an interesting material for this research area.<sup>[41]</sup>

Furthermore, Bahnemann *et al.* showed in 2011, that photoexcited electrons stored in TiO<sub>2</sub> colloids can reduce N<sub>2</sub>.<sup>[12]</sup> Therefore, a similar experiment with the as-synthesized TiO<sub>2</sub> aerogel was performed. 100 mg of the as-synthesized aerogel sample was dispersed in 150 mL of an aqueous 2.5 mol L<sup>-1</sup> methanol solution and irradiated for 100 min under argon to store electrons in the sample. Subsequently, the lamp was turned off and the gas was switched to nitrogen, flushing through the dispersion for 7 hours. Afterwards, a salicylate test was performed to determine the amount of produced ammonia. **Figure S6** shows the absorbance spectra of this salicylate test. An absorbance peak is visible after the reaction time of 7 hours, which related to an obtained ammonia yield of 5  $\mu\text{g L}^{-1}$ . This positive test for dark nitrogen reduction reaction with stored photogenerated electrons on an as-synthesized TiO<sub>2</sub> aerogel sample gives rise to future research work on such aerogels for photocatalytic ammonia generation.

### 3. Conclusion

Mesoporous TiO<sub>2</sub> aerogels with large surface areas were prepared *via* acid-catalyzed sol-gel synthesis and supercritical drying. As-synthesized and calcined TiO<sub>2</sub> aerogels at 300, 400 and 500 °C exhibit surface area of 642, 184, 118 and 92 m<sup>2</sup> g<sup>-1</sup>, respectively. Interestingly, even without calcination, the as-synthesized aerogel is partly crystalline with anatase crystallites.

Increasing the calcination temperature to 500 °C results in decreased surface area, however in strongly increased hydrogen evolution rates in photocatalytic experiments. Here, the crystallinity of the aerogel is the major factor influencing the hydrogen evolution rate.

Moreover, TiO<sub>2</sub> aerogels are able to store photogenerated electrons in surface trap states upon illumination in water-methanol dispersions. The capacity to store photogenerated electrons increases with lower calcination temperature. Furthermore, the extent of electron storage also depends on the methanol scavenger concentration. Finally, nitrogen reduction to ammonia in the dark was performed with photo-generated stored electrons in TiO<sub>2</sub> aerogels, separating the charge carrier photogeneration from the nitrogen reduction reaction. This result paves the way for future application of such tailored and cheap TiO<sub>2</sub> aerogels in solar fuel-on-demand processes.

### 4. Experimental Section

**Chemicals:** Titanium (IV) tetraisopropoxide (98%, Merck), hydrochloric acid (37%, ACS reagent, Sigma Aldrich), ethanol (Chemcolute, denatured with MEK, IPA, and Bitrex, 99.8%), methanol (99.9%, Fisher chemical), hexachloroplatinate (IV) hydrate (99.995%, Carl Roth) were used as received.



*TiO<sub>2</sub> aerogel synthesis:* TiO<sub>2</sub> gels were prepared with acid (HCl) catalyzed sol-gel method using titanium (IV) isopropoxide (TTIP) as precursor. The molar ratio of TTIP/ethanol/acid/water was kept constant 1 : 26 : 0.1 : 4. A solution containing TTIP in ethanol (EtOH) was prepared under magnetic stirring at 0 °C. Hydrochloric acid was added after few minutes. Deionized water was added dropwise to the solution. A gel formed after few minutes. Gels were aged for 7 days at 50 °C, then washed in isopropanol four times and dried with CO<sub>2</sub> at supercritical conditions (60 °C, 115 bar, flow rate 15-20 kg/h). As formed aerogels, excluding as-synthesized aerogel, were thermally treated in air at 300 °C, 400 °C, and 500 °C for 10 h and cooled down to room temperature. The heating rate was set to 10 K min<sup>-1</sup>.

*Characterization methods:* XRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-K<sub>α</sub> radiation source and Lynxeye XE-T detector. The diffraction data were collected in the range of 15-90° 2θ with a step size of 0.01°. The crystallite sizes were estimated using Bruker EVA software by calculating the integral breadth from XRD pattern.

The specific surface area was determined via N<sub>2</sub> physisorption measurements at 77 K on a Micromeritics 3Flex instrument in a partial pressure range of 0.1 < p/p<sup>0</sup> < 0.3 using the Brunauer-Emmett-Teller (BET) method. The total pore volume of the samples were obtained from the N<sub>2</sub> desorption isotherms at a partial pressure of 0.98, and the pore size distribution was obtained using Barrett-Joyner-Halenda (BJH) model. Prior to physisorption analysis, the samples were outgassed at 60 °C for 12 h on a Micromeritics VacPrep Gas Adsorption Sample Preparation Device.

SEM images were taken with a Zeiss Ultra 55 electron microscope using an accelerating voltage of 3-5 kV. The samples were coated with platinum using a Baltec sputter coater prior to measuring.

TEM analysis was performed with a Philips Tecnai F30 operated at 300 kV. D-spacing was determined from TEM images using ImageJ.

A PerkinElmer Lambda 750 UV/vis/NIR spectrometer, equipped with a Praying-Mantis mirror unit from Harrick, was used to record the diffuse reflectance of the powdered aerogels with a step size of 1 nm. The used white standard was a spectralon pellet. The spectra were converted into absorption spectra using Kubelka-Munk function. Tauc plots were used to estimate the band gaps. For the estimation of the absorbance of the dispersions, the spectrometer was equipped with an integrating sphere, and the dispersion was stirred during the measurements of the diffuse reflectance. The spectra were converted to absorbance spectra. Three

measurements were performed for every point and error was determined.

*Photocatalytic test experiments:* For all photocatalytic experiments ultrapure water with TOC = 2 ppb was used. The experiments were conducted with a 300 W AM 1.5G solar simulator equipped with a Xe lamp (Quantum Design) in a top-irradiated glass reaction vessel. Measurements were all performed at 20 °C (ECO RE 1050G (Lauda) thermostat) under stirring. The system was flushed with argon 5.0 before the measurements to remove residual air. Detection of the evolved hydrogen was performed every 11 minutes using a GC2014 gas chromatograph from Shimadzu, equipped with a shin carbon ST column (Restek) and a thermal conductivity detector, using argon 5.0 as carrier gas. The argon 5.0 flow rate for the measurements was set to 25 mL min<sup>-1</sup> with a Bronkhorst mass flow controller.

The hydrogen evolution experiments with Pt photodeposition were carried out with 100 mg aerogel sample dispersed in a mixture of 135 mL water and 15 mL methanol. The dispersion was irradiated for 100 min without co-catalyst. The lamp was turned off and it was waited until no hydrogen evolution was detected anymore, then an aqueous solution of hexachloroplatinate (IV) hydrate was added via rubber sealing without opening the reactor to reach 0.0076 μmol m<sup>-2</sup>. The lamp was turned on again after the hydrogen evolution peak, and the sample was irradiated for another 100 min. Afterwards the lamp was turned off, and it was waited that the hydrogen evolution was zero. Another amount of hexachloroplatinate (IV) hydrate was added to the calcined aerogel dispersion to reach the same amount of 0.1 wt.-% Pt as for the as-synthesized aerogel sample. The dispersions of the calcined aerogel samples were irradiated again for 100 min, the lamp was turned off and the measurements were stopped after no hydrogen evolution was detected. Photographs of all dispersions were taken before the measurement and after each irradiation step. The samples with Pt deposited were washed with isopropanol three times and centrifuged at 1500 rpm. Then they were dried with CO<sub>2</sub> at supercritical conditions. XRD measurements were performed as described above to determine any changes on the sample.

For the experiments to detect the absorbance of the dispersions, 100 mg of the aerogel sample were dispersed in a mixture of 135 mL of water and 15 mL methanol. After flushing with argon 5.0, a sample of approximately 2.5 mL dispersion was taken and filled in a flushed closed cuvette, and the diffuse reflectance was measured in a PerkinElmer Lambda 750 UV/vis/NIR spectrometer, equipped with an integrating

sphere under stirring. The aerogel dispersions were afterwards irradiated for 100 min. 2.5 mL of the blueish dispersion was filled in an argon flushed cuvette and the diffuse reflectance was measured immediately, 30 minutes, and 110 min after the sample was taken.

For the experiments of the dependency of the electron storage ability on the methanol concentration, 100 mg of the as-synthesized aerogel sample were dispersed in 150 mL aqueous methanol solutions with different methanol concentrations ranging from 0.02 mol L<sup>-1</sup> up to 19.7 mol L<sup>-1</sup>. The dispersions were irradiated for 100 min. Photographs of the dispersions were taken directly after the irradiation.

For the nitrogen reduction reaction, 100 mg of the as-synthesized aerogel was dispersed in 150 mL of 2.5 mol L<sup>-1</sup> aqueous methanol solution. The dispersion was irradiated for 100 min under the same conditions as for the absorbance detection measurements, the argon 5.0 flow rate was set to 50 mL min<sup>-1</sup>. After the irradiation under argon 5.0, the carrier gas was switched to N<sub>2</sub>. The flow rate was set to 50 mL min<sup>-1</sup> N<sub>2</sub> for 7 h for the nitrogen reduction reaction in the dark. Afterwards a salicylate test was performed to determine the yield of NH<sub>3</sub>.<sup>[42]</sup>

## Acknowledgements

We thank Judith Zander (University of Bayreuth) for support in the NRR experiment and Markus Heyer (DLR) for support in supercritical drying.

## Conflict of interest

The authors declare no conflict of interest.

## References

- [1] N. Hüsing, U. Schubert, *Angew. Chemie - Int. Ed.* **1998**, *37*, 22–45.
- [2] S. Alwin, X. Sahaya Shajan, *Mater. Renew. Sustain. Energy* **2020**, *9*, 3.
- [3] K. C. Song, S. E. Pratsinis, *J. Am. Ceram. Soc.* **2001**, *84*, 92–98.
- [4] H. Choi, M. Carboni, Y. K. Kim, C. H. Jung, S. Y. Moon, M. M. Koebel, J. Y. Park, *Catal. Letters* **2018**, *148*, 1504–1513.
- [5] H. Schäfer, B. Milow, L. Ratke, *RSC Adv.* **2013**, *3*, 15263–15272.
- [6] S. Sadriyeh, R. Malekfar, *J. Non. Cryst. Solids* **2017**, *457*, 175–179.
- [7] M. L. Anderson, R. M. Stroud, C. A. Morris, C. I. Merzbacher, D. R. Rolison, *Adv. Eng. Mater.* **2000**, *2*, 481–488.
- [8] P. A. DeSario, J. J. Pietron, D. H. Taffa, R. Compton, S. Schünemann, R. Marschall, T. H. Brintlinger, R. M. Stroud, M. Wark, J. C. Owrutsky, D. R. Rolison, *J. Phys. Chem. C* **2015**, *119*, 17529–17538.
- [9] Y. Di Iorio, M. E. Aguirre, M. A. Brusa, M. A. Grela, *J. Phys. Chem. C* **2012**, *116*, 9646–9652.
- [10] D. A. Panayotov, P. A. Desario, J. J. Pietron, T. H. Brintlinger, L. C. Szymczak, D. R. Rolison, J. R. Morris, *J. Phys. Chem. C* **2013**, *117*, 15035–15049.
- [11] M. Sachs, E. Pastor, A. Kafizas, J. R. Durrant, *J. Phys. Chem. Lett.* **2016**, *7*, 3742–3746.
- [12] D. Bahnemann, A. Henglein, J. Lilie, L. Spanhel, *J. Phys. Chem.* **1984**, *88*, 709–711.
- [13] H. H. Mohamed, R. Dillert, D. W. Bahnemann, *J. Phys. Chem. C* **2011**, *115*, 12163–12172.
- [14] H. H. Mohamed, R. Dillert, D. W. Bahnemann, *Chem. - A Eur. J.* **2012**, *18*, 4314–4321.
- [15] H. H. Mohamed, R. Dillert, D. W. Bahnemann, *J. Photochem. Photobiol. A Chem.* **2011**, *217*, 271–274.
- [16] H. H. Mohamed, R. Dillert, D. W. Bahnemann, *J. Photochem. Photobiol. A Chem.* **2012**, *245*, 9–17.
- [17] H. H. Mohamed, C. B. Mendive, R. Dillert, D. W. Bahnemann, *J. Phys. Chem. A* **2011**, *115*, 2139–2147.
- [18] M. Sakar, C. C. Nguyen, M. H. Vu, T. O. Do, *ChemSusChem* **2018**, *11*, 809–820.
- [19] C. Ng, A. Iwase, Y. H. Ng, R. Amal, *ChemSusChem* **2013**, *6*, 291–298.
- [20] M. Schulz, N. Hagmeyer, F. Wehmeyer, G. Lowe, M. Rosenkranz, B. Seidler, A. Popov, C. Streb, J. G. Vos, B. Dietzek, *J. Am. Chem. Soc.* **2020**, *142*, 15722–15728.
- [21] V. W. Lau, B. V. Lotsch, *Adv. Energy Mater.* **2021**, 2101078.
- [22] J. Kröger, A. Jiménez-Solano, G. Savasci, P. Rovó, I. Moudrakovski, K. Küster, H. Schlömerberg, H. A. Vignolo-González, V. Duppel, L. Grunenberg, C. B. Dayan, M. Sitti, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, *Adv. Energy Mater.* **2021**, *11*, DOI 10.1002/aenm.202003016.
- [23] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, **2015**, DOI 10.1515/pac-2014-1117.
- [24] C. Schlumberger, M. Thommes, *Adv. Mater. Interfaces* **2021**, *8*, 2002181.
- [25] R. Bardestani, G. S. Patience, S. Kaliaguine, *Can. J. Chem. Eng.* **2019**, *97*, 2781–2791.
- [26] P. Voepel, M. Weiss, B. M. Smarsly, R. Marschall, *J. Photochem. Photobiol. A Chem.* **2018**, *366*, 34–40.
- [27] C. C. Lin, T. Y. Wei, K. T. Lee, S. Y. Lu, *J. Mater. Chem.* **2011**, *21*, 12668–12674.
- [28] C. Dette, M. A. Pérez-Orsorio, C. S. Kley, P. Punke, C. E. Patrick, P. Jacobson, F. Giustino, S. J. Jung, K. Kern, *Nano Lett.* **2014**, *14*, 6533–6538.
- [29] D. Zywitzki, H. Jing, H. Tüysüz, C. K. Chan, *J. Mater. Chem. A* **2017**, *5*, 10957–10967.
- [30] J. Kiwi, M. Grätzel, *J. Phys. Chem.* **1984**, *88*, 1302–1307.
- [31] A. Furube, T. Asahi, H. Masuhara, H. Yamashita, M. Anpo, *Chem. Phys. Lett.* **2001**, *336*, 424–430.
- [32] S. Ikeda, N. Sugiyama, S. Murakami, H. Kominami, Y. Kera, H. Noguchi, K. Uosaki, T. Torimoto, B. Ohtani, *Phys. Chem. Chem. Phys.* **2003**, *5*, 778–783.
- [33] M. Kong, Y. Li, X. Chen, T. Tian, P. Fang, F. Zheng, X. Zhao, *J. Am. Chem. Soc.* **2011**, *133*, 16414–16417.
- [34] J. Yan, G. Wu, N. Guan, L. Li, Z. Li, X. Cao, *Phys. Chem. Chem. Phys.* **2013**, *15*, 10978.

- [35] C.-C. Lin, T.-Y. Wei, K.-T. Lee, S.-Y. Lu, *J. Mater. Chem.* **2011**, *21*, 12668.
- [36] A. S. Cherevan, L. Deilmann, T. Weller, D. Eder, R. Marschall, *ACS Appl. Energy Mater.* **2018**, *1*, 5787–5799.
- [37] A. Hofmann, M. Weiss, J. Timm, R. Marschall, *Adv. Mater. Interfaces* **2021**, *8*, DOI 10.1002/admi.202100813.
- [38] A. Hofmann, M. Weiss, R. Marschall, *J. Phys. Energy* **2021**, *3*, 14002.
- [39] D. Ziegenbalg, J. Zander, R. Marschall, *ChemPhotoChem* **2021**, *5*, 792–807.
- [40] M. Cheng, C. Xiao, Y. Xie, *J. Mater. Chem. A* **2019**, *7*, 19616–19633.
- [41] C. Li, T. Wang, Z.-J. Zhao, W. Yang, J.-F. Li, A. Li, Z. Yang, G. A. Ozin, J. Gong, *Angew. Chemie* **2018**, *130*, 5376–5380.
- [42] L. Zhou, C. E. Boyd, *Aquaculture* **2016**, *450*, 187–193.



## Supporting Information

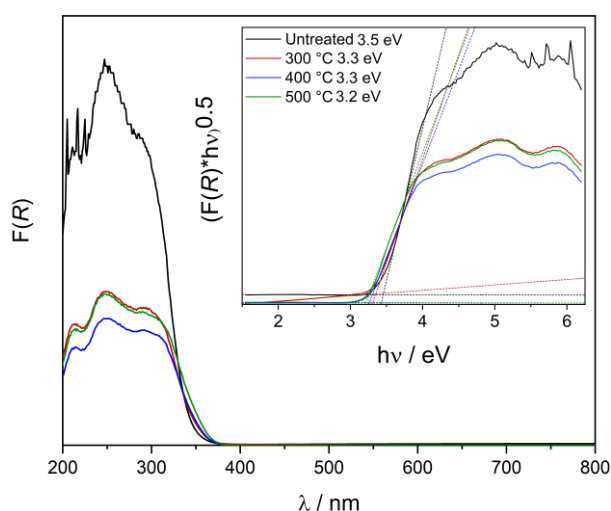
### Photocatalytic activity and electron storage ability of TiO<sub>2</sub> aerogels with adjustable surface area

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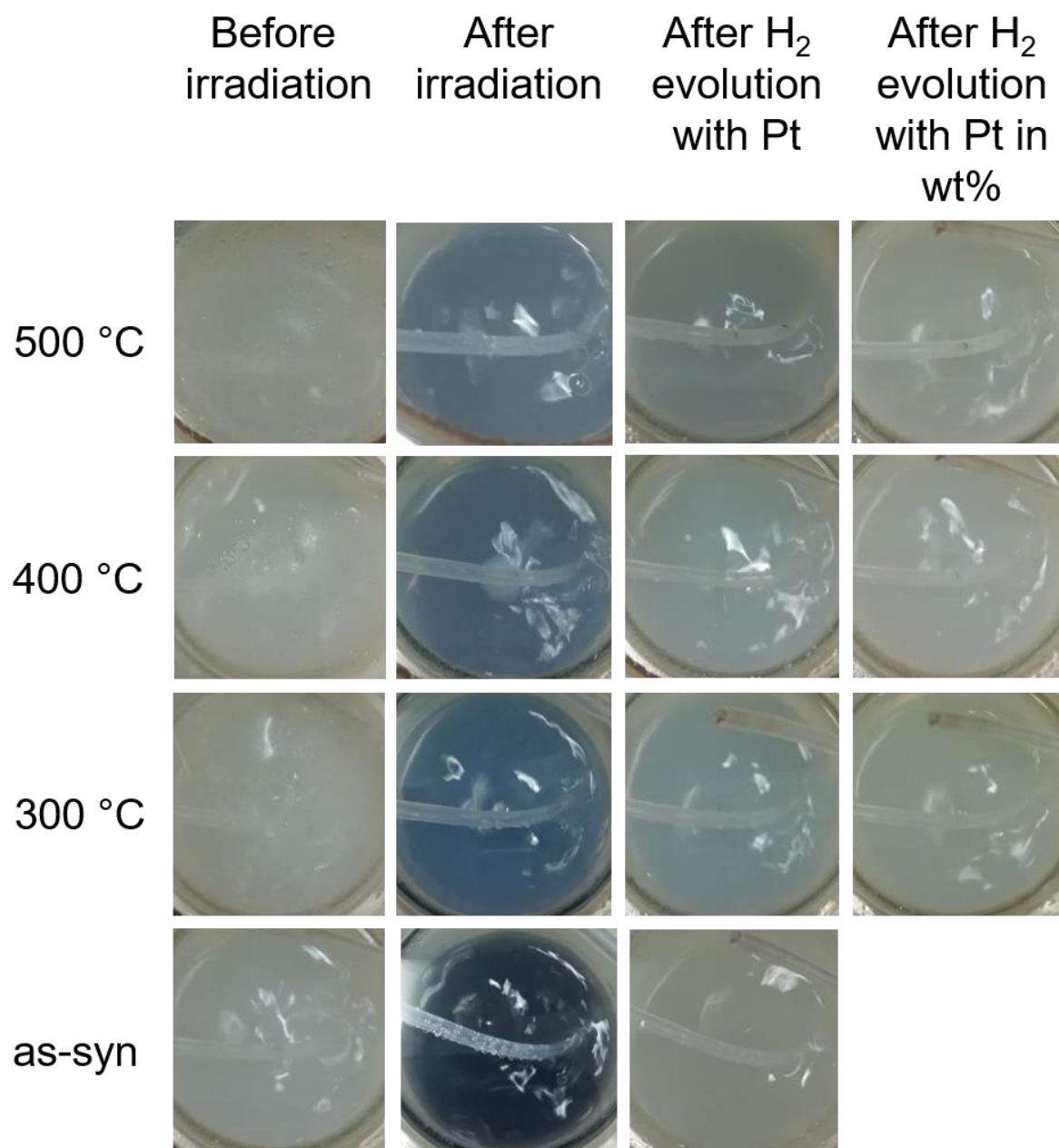
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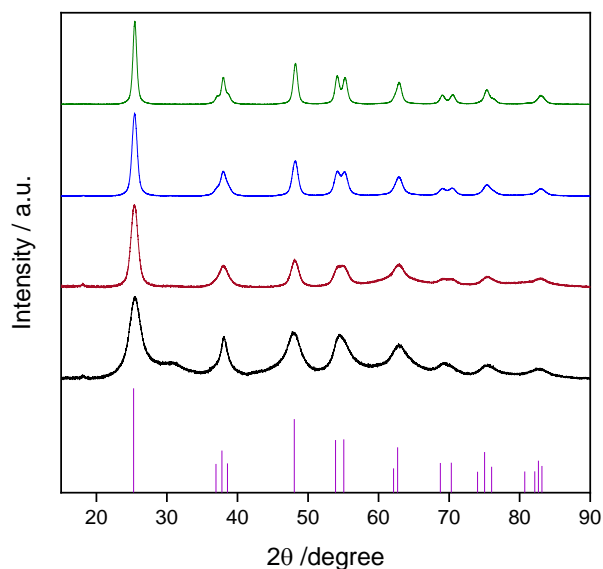
§: These authors contributed equally to the manuscript.



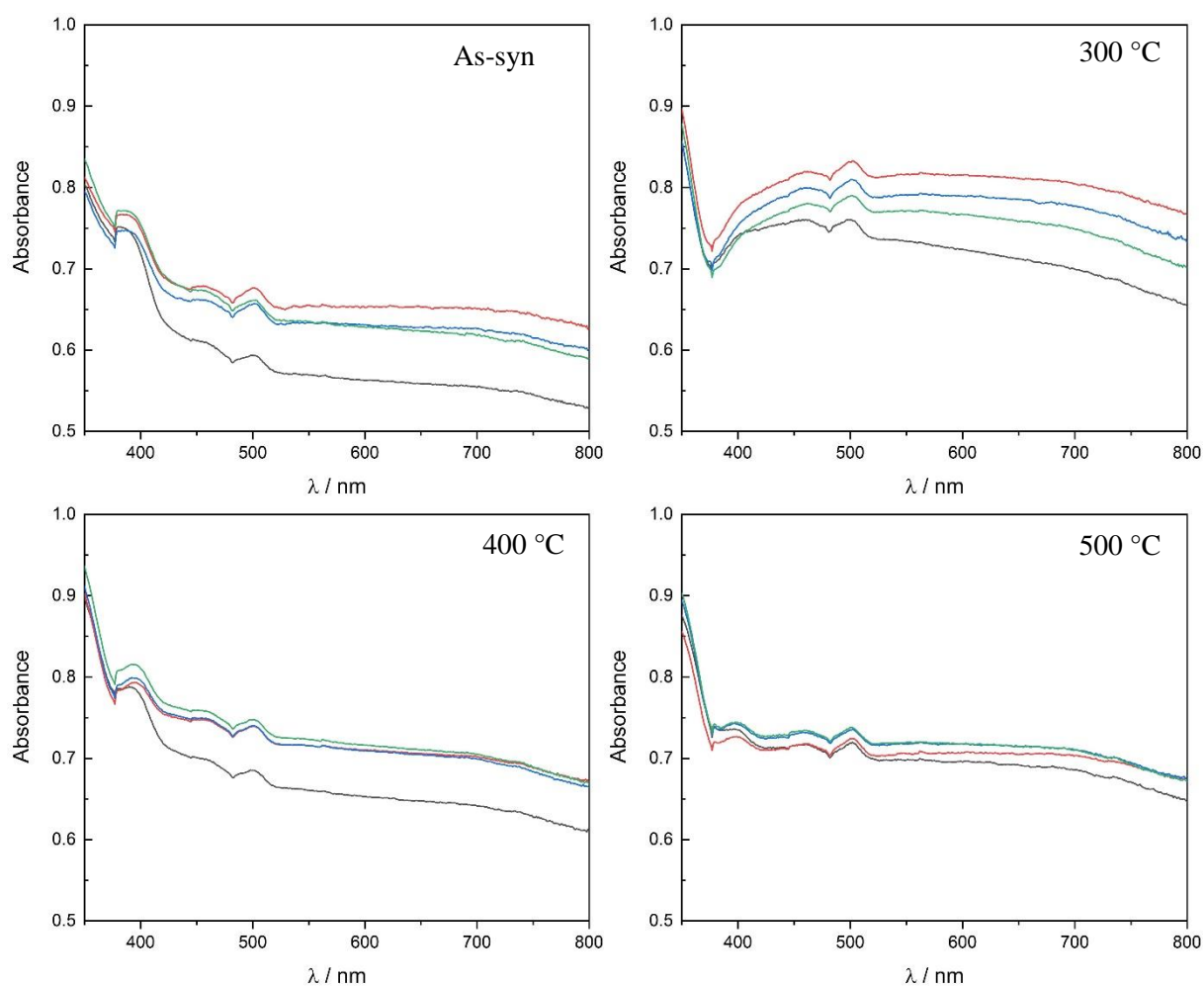
**Figure S1.** Kubelka-Munk UV-vis spectra and Tauc plots (inset) of the as-synthesized aerogel (black), the 300 °C (red), the 400 °C (blue), and the 500 °C (green) calcined aerogels.



**Figure S2:** Enlarged photographs from Figure 5, showing the coloration of the different photocharged aerogel dispersions.



**Figure S3.** XRD patterns of the as-synthesized TiO<sub>2</sub> aerogel (black) and aerogels calcined at 300 °C (red), 400 °C (blue) and 500 °C (green) after photocatalytic hydrogen production reaction. Reference pattern of anatase TiO<sub>2</sub> (PDF-21-1272) is shown for comparison. Normalized data to the range 0 to 100 related to the highest signal.



**Figure S4.** Absorbance measurements of the four TiO<sub>2</sub> aerogels dispersions, before irradiation (gray), directly after 100 min of irradiation (green), 30 min after irradiation (blue) and 1 h 50 min after irradiation (red).





0.02 mol/L



1.2 mol/L



1.8 mol/L



2.5 mol/L



4.9 mol/L

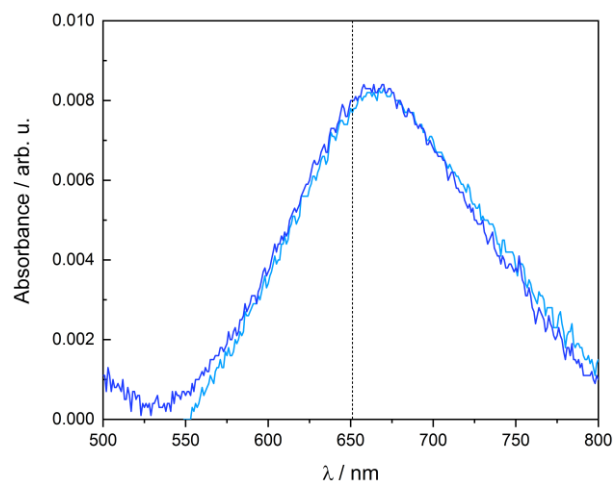


9.9 mol/L



19.7 mol/L

**Figure S5:** Enlarged photographs of photocharged  $\text{TiO}_2$  aerogel dispersion with different MeOH concentration in water.



**Figure S6.** Absorbance spectra of the salicylate test of the solution of nitrogen reduction reaction with and as-synthesized  $\text{TiO}_2$  aerogel sample for determination of the obtained  $\text{NH}_3$  concentration. The test was performed two times to verify the result. The dashed line is the absorbance maximum, which was used for the calibration.