

Water Splitting and Electricity with Semiconducting Silicides in Sunlight

M. Demuth, K. Kerpen, A. Kuklya, M.-A. Wüstkamp

This document appeared in

Detlef Stolten, Thomas Grube (Eds.):

18th World Hydrogen Energy Conference 2010 - WHEC 2010

Parallel Sessions Book 3: Hydrogen Production Technologies - Part 2

Proceedings of the WHEC, May 16.-21. 2010, Essen

Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-3

Institute of Energy Research - Fuel Cells (IEF-3)

Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010

ISBN: 978-3-89336-653-8

Water Splitting and Electricity with Semiconducting Silicides in Sunlight

Martin Demuth, Max-Planck-Institut für Bioanorganische Chemie, D-45413 Mülheim an der Ruhr, Germany and H2 Solar GmbH, D-79541 Lörrach, Germany

Klaus Kerpen, Andriy Kuklya, Marc-Andre Wüstkamp, Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim an der Ruhr, Germany

Abstract

Generation of hydrogen and oxygen from water is described using mainly the semiconductor titanium disilicide as catalyst and halogen light which closely mimics solar radiation. The reactions are carried out under non-aerobic conditions, i.e., under nitrogen. High efficiencies are reached at 1.1-1.2 bar pressure. In the first phase of these reactions the catalytically active centers are built up. During this phase of reaction the kinetics of the water splitting process is growing in and leads to a linear dependence in the further course of the reactions which consists of >96% water splitting to yield hydrogen and oxygen in a 2:1 ratio. Hydrogen is partially and reversibly stored physically, depending on temperature. Oxygen behaves differently since it is stored entirely under the applied reaction conditions (50-80 °C and light) and can be liberated from storage upon heating the slurries in the dark. This allows convenient separation of hydrogen and oxygen. The stability of titanium disilicide has been positively tested over several months. This material is abundant and inexpensive besides that it absorbs most of the solar radiation. Further, XRD and XPS studies show that titanium disilicide is 80% crystalline and the oxide formation is limited to a few molecular layers in depth. By using labeled water it was shown that labeled dioxygen appears in the gas phase of such reactions, this showing definitively that hydrogen evolution occurring here stems from photochemical splitting of water.

Further, water splitting is part of a project which involves photoelectrochemistry and in which the silicides are used as light-receiving electrode and transition metal-coated anodes serve to split water.

Key words: Solar hydrogen and oxygen; water splitting; semiconductor photocatalysis; titanium disilicide; oxygen storage; hydrogen storage, photoelectrochemistry.

1 Water Splitting, i.e. Hydrogen and Oxygen Evolution from Water Using Silicide Catalysts as Powders and Solar Light

Hydrogen and oxygen production from water with semiconductors and light is an important issue in the exploitation of solar radiation² as a sustainable energy. However, a major drawback of most of the research in this field relates to the fact that appropriate semiconductors either are not readily accessible, absorb solar radiation inefficiently,³⁻⁸ or produce hydrogen in a sacrificial manner only. We present here the use of titanium silicides, Ti_5Si_3 and TiSi_2 , as prototypes for a promising new class of semiconductors which so far have not been used for the title application. These materials are inexpensive and abundant, and

they absorb solar radiation efficiently. A major point concerns the stability of these alloys in water, which could have been questioned a priori.^{9,10} However, we anticipated that sufficiently effective passivation of the titanium silicides by a finite oxide layer might be the clou to render this project successful.¹¹

The absorption characteristics of these materials are ideal for solar application: broad band reflectance measurements show a band gap range from 3.4 eV (ca. 360 nm) to 1.5 eV (ca. 800 nm) for TiSi₂. This is atypical of semiconductors since these materials usually exhibit little band gap spreads. Determination of the quasi-Fermi level of electrons at pH 7 afforded a value of -0.43 eV and -0.41 eV for both silicides before and after reaction, respectively.¹²

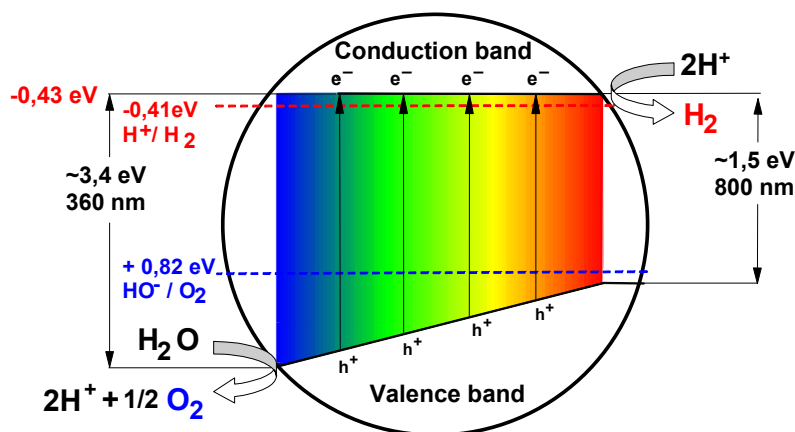
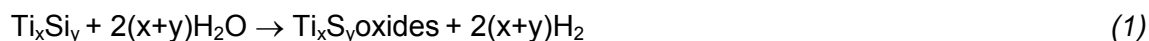


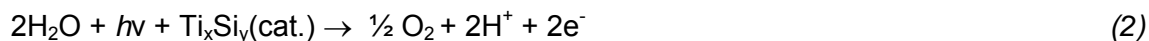
Figure 1: Band-gap range of the titanium silicide photocatalysts employed in this work.

Suspensions of titanium silicide alloys in either tridistilled or tap water, both giving identical results, at pH 7 were irradiated at 50 to 60 °C in round-bottomed flasks or cylindrical glass vessels which were equipped with a gently stirring magnetic bar and which were either closed or connected to a gas burette (*standard conditions*). In both cases non-aerobic conditions were applied, i.e., the reactions were run under nitrogen after purging the water with nitrogen. Externally positioned halogen lamps with wavelength emissions closely mimicking solar radiation served as light source with an emission range of 310-800 nm (main range at 380-780 nm). The resulting gas evolution (hydrogen and dioxygen) was monitored by gas chromatography (gc; TCD detector; column: Rt-Msieve 13X, 30 m, S-40); nitrogen served as reference gas. The gas partial pressure of the closed reactions was normalized at intervals. The majority of the reactions was run with TiSi₂ (2 g,¹³ supplier Alfa; in 150 ml water), 100% light absorption and 26 cm² surface of irradiation); Ti₅Si₃ showed lower catalytic activity and was therefore used for exploratory experiments only.

Two rates for hydrogen evolution are observed at 55-60 °C: One for the *thermally driven reduction/addition of water to the titanium silicide giving limited amounts of sacrificially formed hydrogen* according to



during the initial phase A (Figure 2). This process is in part responsible for the in situ formation of the catalytically active domains (see discussion below) at both, the silicon and titanium of the alloy. Its rate depends strongly on the quality of the catalyst, temperature and pH.¹⁴ The second rate (phase B) stands for oxygen and hydrogen formation in the *light-driven water splitting process*



together with the exothermic *reduction of the protons* formed in (2):



Hydrogen. Phase A of hydrogen evolution (Figure 2) starts at time = 0 with $\text{conc.}(\text{H}_2) = 0$ and shows a non-linear grow-in dependence. Phase B is characterized by the linear part of the hydrogen evolution curve. We interpret the time dependence of hydrogen evolution as a consequence of simultaneously occurring reactions (1)-(3) [for illustration of the processes (1)-(3), see Figure 4]. The thermal reaction (1) alone has initially a similar dependence but it levels off and does not yield the linear part of phase B which has been verified by dark reactions under the same conditions. At 55-60 °C under nitrogen phase A is distinctly replaced by phase B (Figure 2). This shows the existence of at least two processes being responsible for hydrogen production. According to our interpretation the catalytically active domains for water splitting are built up within phase A via (1) together with the growing-in processes (2) + (3) being essential for the activity of the catalytic domains; these are seemingly not formed in dark reactions (see above). Only minor water splitting is found in phase A (cf. run 1 in Table 1 yielding a minor amount of oxygen only) besides major sacrificial hydrogen formation via (1) which ceases at the end of phase A. Notably, the initially formed volume of sacrificial hydrogen remains unchanged, within exptl. error, thereafter (cf. runs 2-5 in Table 1) and >96% pure water splitting controls phase B. In a parallel run at 50 °C under nitrogen (Figure 3) the change of kinetics is not as significant as at 55-60 °C since the rate of formation of sacrificial hydrogen is lower. The limited growth of the catalytically active domains is controlled by temperature and pH.¹⁴

A significant increase of the water splitting rate is found at higher gas pressure as shown in Figure 3 (standard conditions, closed vessel) reaching energy conversions (η) of 4% (at rates β and γ in Figure 3).

A technically important aspect of titanium silicide semiconductors is the capacity for reversible physical hydrogen storage (for oxygen storage, see below). The hydrogen storage capacity of, e.g., ca. 20 ml $\text{H}_2/\text{g TiSi}_2$ at 30 °C and ca. 5-7 ml $\text{H}_2/\text{g TiSi}_2$ at 50 °C is certainly lower than the one encountered for other inorganic materials forming metal hydrides which, however, are technically more demanding and require higher reaction temperatures.¹⁵ Nevertheless the hydrogen storage capacity of TiSi_2 is sufficient for short term storage and it minimizes undesired overpressure during reaction.

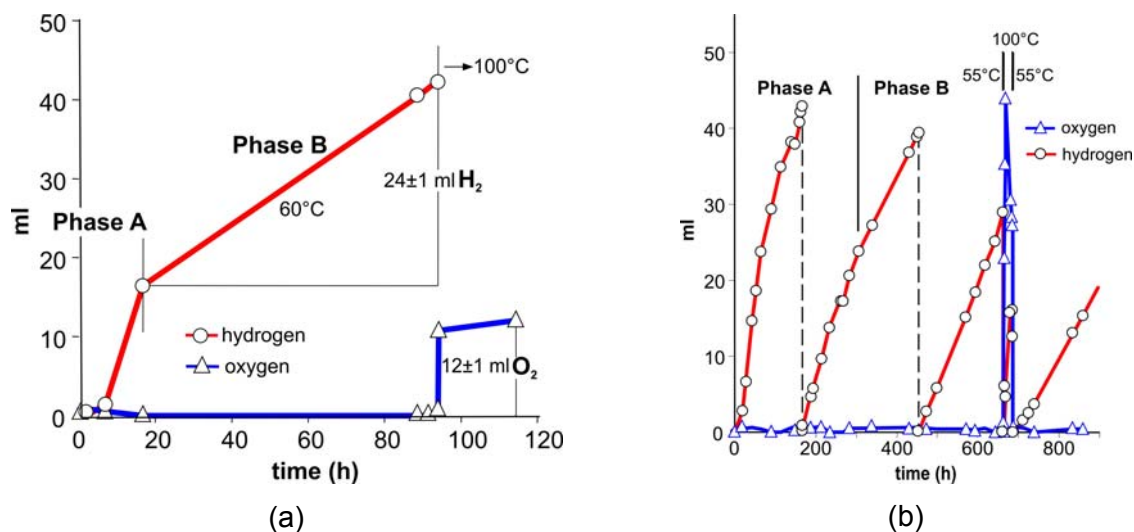


Figure 2: Representative reactions at 60 (a) and 55 °C (b) under nitrogen. Phase-A hydrogen evolution (red): formation of the catalytic domains (cd, Figure 4) and growing in of the water splitting kinetics (2) + (3). Dashed lines: pressure release and flushing the gas phase with nitrogen (scale shift of hydrogen concentration to 0). Phases B: hydrogen evolution from water splitting (>96% by comparison with dark reactions) showing linear kinetics. Liberation of dioxygen (blue) from storage upon heating to 100 °C in the dark [cf. (a), (b) and runs 3, 5 in Table 1, respectively].

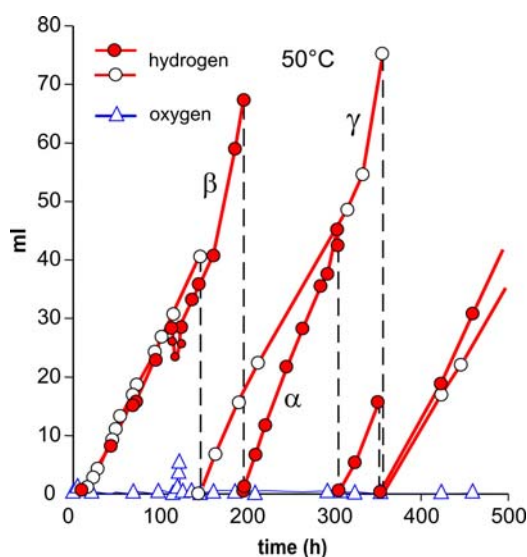


Figure 3: Pressure dependent efficiency of water splitting as determined by hydrogen evolution measurement (reactions under nitrogen). Dashed lines: pressure release and flushing the gas phase with nitrogen (scale shift of hydrogen concentration to 0). Efficiency (η) = 4 % (at rates β and γ). β and γ rates are obtained at 1.1-1.2 bar. The reactions were run at 50 °C and in one example oxygen was released from storage in phase A after ca. 125 h by short heating to 100 °C in the dark (4x amplification of peak intensity; cf. run 1 in Table 1); thereafter the reaction was continued at 50 °C.

Oxygen. The evolution of oxygen requires further comment since in routine runs at constant temperature only hydrogen is found in the gas phase, and dioxygen does not appear. Also there is no hydrogen peroxide detected in either gas and liquid phase. As it turned out, oxygen is stored efficiently by the titanium silicide catalyst and the conditions for its release from storage are different from those of hydrogen. A quantitative release of dioxygen sets in rapidly when reaction slurries are heated to ≥ 100

$^{\circ}\text{C}$ in the dark (see Figures 2, 3 and Table). An H_2/O_2 ratio of 2:1 for the water splitting process in phase B results, which is compatible with our claim that phase B-hydrogen and -dioxygen production is catalytic. This result exemplifies for the first time liberation of stored dioxygen from a semiconductor surface.¹⁶

A mechanistic picture regarding this particular behaviour of oxygen is still open to speculation. It could have been argued that oxygen is stored at the site where water splitting occurs, i.e., in the catalytic oxide domains [(cd) in II and III in Figure 4)]. However, these catalytic domains are unlikely the storage site for oxygen from (2), since its uptake by the catalyst occurs very efficiently from time = 0.¹⁷ In this connection it is of interest to compare our result with a recent study of the adsorption of oxygen in the course of its photoreduction at a TiO_2 surface, employing ab initio calculations based on infrared data.¹⁸ It was concluded that desorption of (ionized) oxygen is hardly possible from the surface of such a gas-solid system. Another investigation supports our finding in that a high storage capacity of TiO_2 for oxygen (25 wt%) is found upon high-temperature treatment;¹⁶ an equilibrium between TiO_2 and a lower oxide is proposed as oxygen trap in analogy to CeO_2 .¹⁹ We favor the idea that in our system water-solubilized dioxygen leaves the catalytic domain after photolytic water splitting (III in Figure 4) and is stored thereafter under irradiation in clusters (IV in Figure 4) at the oxide layer of the catalyst formed upon oxygen addition to titanium silicide from moisture prior to submersion in water (I in Figure 4). The clusters would then release dioxygen at 100°C .

Table 1: Analysis of the gas phase by gaschromatography.

Run	H_2 (total in the gas phase, ml)	O_2 (evolved from storage, ml) ^a	H_2 [thermal from (1)](ml) ^b	H_2 [from water splitting (2) + (3)] (ml) ^c
1	6	< 3 d,e	< 6	< 6
2	24	5 e	14	10
3	40	12 e	16	24
4	42	15 e	12	30
5	112	48 e	16	96

^a Gas phase + 3 ml dissolved in water; ^b H_2 (total) - H_2 (splitting); ^c calc: ml $\text{O}_2 \times 2$; ^d below detection limit in gas phase; ^e unloaded from storage upon heating to 100°C in the dark. Exptl. error 5-10 %.

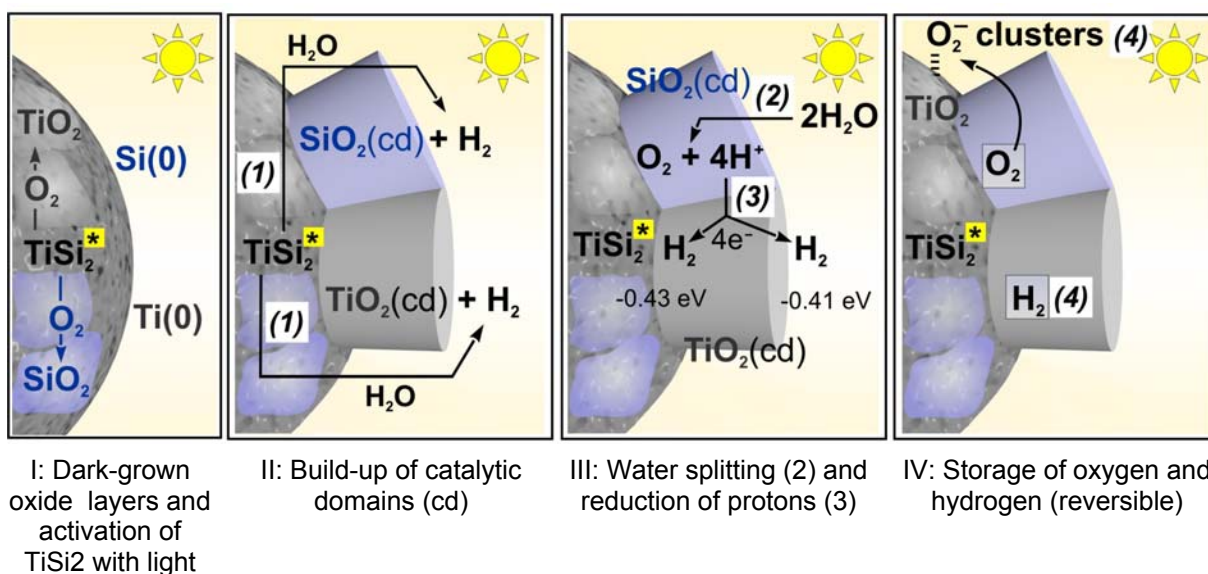


Figure 4: Proposed mechanistic events. TiSi₂*: electronically excited TiSi₂ by solar radiation (mimicked in this work by halogen light), surface partially covered by TiO₂ and SiO₂ layers originating from oxidation of TiSi₂ by moisture prior to water contact under irradiation (I); build up of catalytically active domains in water (1) under irradiation and nitrogen at 50-60 °C (thermal and photochemical) (II); (2) water splitting ($\rightarrow \text{O}_2 + 4\text{H}^+$) (photochemical); (3) reduction of $2\text{H}^+ \rightarrow 2\text{H}^\bullet \rightarrow \text{H}_2$ (thermal) (III); (4) reversible storage of H₂ and O₂ (thermal) and formation of O₂⁻ clusters (photochemical) (IV).

XRD and XP Spectroscopy. The aforementioned slight decrease of the reduction potential of the titanium silicides to 4.1 ± 0.1 eV at pH 7 during reaction points to the formation of titanium oxide layers or domains the potential of which is comparable with the one of TiO₂²⁰ (Figure 4). X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) of the structural changes of TiSi₂ in

water and upon irradiation revealed intricate insights. An average sample of TiSi₂ shows 80% crystalline and 20% amorphous phase as determined by XRD. No changes of the XRD pattern are detectable even after longer reaction times of the catalyst. Also the XPS relative peak intensities of the TiSi₂ samples remain constant after reaction times of 100-200 h. Both composite regions of the TiSi₂ are covered in part by an oxide layer and, interestingly, even after extended reaction times Ti(0) and Si(0) domains remain detectable by XPS. The oxide layers and domains, as measured for both titanium and silicon by XPS sputtering technique, are limited to a few molecular layers in depth.

In conclusion we consider the *in situ* grown catalytic domains TiO₂(cd) on the TiSi₂ binary alloy being responsible for hydrogen formation and the corresponding catalytic domains SiO₂(cd) for the water splitting process (see II and III in Figure 4). Under the applied reaction conditions TiSi₂ does not show detectable instability during phase-B water splitting over several months; hence long-lasting stability can be predicted. The hydrogen production by water splitting under the non-optimized laboratory conditions described, amounts to 20-25 ml per 26 cm² irradiated area at 1.1-1.2 bar and per 24 h using low-power halogen lamps, the

light intensity of which is 3-50 times lower than the total of diffuse and direct solar radiation. This corresponds to an energy conversion (η) for hydrogen formation of 4% wherein the expected high energy content of the compactly stored oxygen is not yet included.²¹ The important result concerning reversible photoadsorption of oxygen at low temperatures allows beneficially convenient separation of the two product gases based on their different physisorption properties.

2 Water Splitting via Photoelectrochemistry – the Silicides Serve as Cathodes

Further, silicides are being explored as photoelectrodes for water splitting and production of electricity via electrochemical photovoltaics [1b]. A prototype of a *photoelectrochemical cell for water splitting* (TriplePowerCell, Picture 1) has been realized, consisting of a silicide cathode and a transition metal counter electrode (e.g. IrO_2). The cathode (silicide for reduction of protons to hydrogen) is the light-receiving electrode and is prepared by sputtering of the silicides on titanium sheets. The counter electrode (transition metal coating of titanium sheets serve for water splitting) is prepared by dipping method. The electrodes are inserted into an electrolyte and are separated by a Nafion membrane for selective proton exchange and for separation of the product gases hydrogen and oxygen. This device (Picture 1, below) can in the future also serve the production of electricity upon proper choice of the electrode potentials and is able to collect residual thermal energy. It is important to note that the silicide materials and counter electrodes employed for the photoelectrochemical applications are thermally (up to at least 300 °C) and mechanically stable besides being corrosion resistant.



Picture 1: TriplePowerCell assembly which adopts a silicide cathode as light receiver and a transition metal anode and is filled with an electrolyte (e.g., water - sulfuric acid or a base or salts). The system is able to a) split water into hydrogen and oxygen under acidic conditions where the product gases can be separated by a membrane, and b) the system allows to collect additionally or separately electricity, and c) the TriplePowerCell allows to collect residual thermal energy by way of a heat exchanger.

Acknowledgment

We thank the *Max Planck Society (Germany)* for generous financial support of this work.

References

- [1] a) Patent: Demuth, M.; Ritterskamp, P., Generation of Hydrogen and Oxygen from Water and Storage thereof with Silicides, no 10 2005 040 255.0 (Germany) and PCT/EP2006/008333. b) German patent application no 10 2008 021 489.2: Demuth, M., Kerpen, K. Kuklya, A., Silicides for Photoelectrochemical Water Splitting and/or Production of Electricity (2008). c) Ritterskamp, P; Kuklya, A.; Wüstkamp, M.-A.; Kerpen, K.; Weidenthaler, C.; Demuth, M. *Angew. Chem. Int. Ed.* 2007, 119, 7917-7921.
- [2] Bard, A. J.; Fox. M. A. *Acc. Chem. Res.* 1995, 28, 141-145.
- [3] Fujishima, A.; Honda, K. *Nature* 1972, 238, 37-38.
- [4] Kato, H.; Kudo, A. *J. Phys. Chem. B* 1972, 106, 5029-5034.
- [5] Sayama, K.; Mukasa, K.; Abe, R.; Abe, Y.; Arakawa, H. *Chem. Comm.* 2002, 2416-2417.
- [6] Maeda, K.; Takata, T.; Hara, M.; Saito, N.; Inoue, Y.; Kobayashi, H.; Domen, K. *J. Am. Chem. Soc.* 2005, 127, 8286-8287.
- [7] Maeda, K.; Teramura, K.; Takata, T.; Hara, M.; Saito, N.; Toda, K.; Inoue, Y.; Kobayashi, H.; Domen, K. *J. Phys. Chem B* 2005, 109, 20504-20510.
- [8] Maeda, K.; Teramura, K.; Lu, D.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. *Nature* 2006, 440, 295.
- [9] a) Murarka, S. P. *Ann. Rev. Mater. Sci.* 1983, 13, 117-137. b) Silicides – Fundamentals and Applications, Miglio, L.; d'Heurle, F. (eds.), World Scientific (Singapore, New Jersey, London, Hong Kong) (2000).
- [10] Murarka, S. P. *Annu. Rev. Mater. Sci.* 1983, 13, 117-137.
- [11] Holleman, A. F.; Wiberg, E.: *Lehrbuch der Anorganischen Chemie/Holleman-Wyberg, de Gruyter* (Berlin, New York), 101st ed., pp. 890ff (1995).
- [12] We thank Professor H. Kisch and Dipl.-Chem. J. Eberl, Dept. of Inorganic Chemistry, University of Erlangen-Nürnberg, Germany, for helpful discussions and the measurements of the quasi-Fermi levels.
- [13] The relatively large amount of TiSi₂ is chosen to provide for sufficient oxygen storage during irradiation. For catalytic purposes alone 20% of this amount is sufficient to overcome the slow water-gas exchange processes at the heterogeneous catalytic site.
- [14] Results to be published and work in progress.
- [15] Bellosta von Colbe, J. M.; Schmidt, W.; Felderhoff, M.; Bogdanovic, B.; Schüth, F. *Angew. Chem Int. Ed.* 2006, 45, 3663-3665.
- [16] Cf. a literature claim of reversible dioxygen storage, not substantiated by experiment except in an indirect disclosure where hydrocarbons are oxidized by oxygen-enriched TiO₂: Sinel'niko, V. V.; Tolkachev, N. N.; Stakheev, A. Y. *Kinetics and Catalysis* 2005, 46, 550-554 and refs. 10-14 cited therein.

- [17] This has been verified by runs under air wherein oxygen uptake under irradiation is constant and fast even from time = 0, i.e., at the onset of formation of the catalytically active domains.
- [18] a) Mattioli, G.; Filipponi, F.; Bonapasta, A. M. J. Am. Chem. Soc. 2006, 126, 13772-13780. b) Gerischer, H.; Heller, A. J. Electrochem. Soc. 1992, 139, 113-118.
- [19] Kaspar, J.; Fornasiero, P.; Hockey, N. Catal. Today 2003, 77, 419.
- [20] Carp, O.; Huisman, C. L.; Reller, A. Progress in Solid State Chemistry 2004, 32, 33-177.
- [21] This result compares favorably with the efficiencies reported for other semiconducting materials used for water splitting with visible light, all having so far drawbacks: One example of 2.5 % efficiency evidently works for short reaction times and within a narrow wavelength range of solar radiation only (ref. 8); all others lie <1 % (refs 7, 22). Further improvement of the photo-electrocatalytic Grätzel multicomponent system (ref. 23) which employs dyes for sufficient light absorption and electrolytes, both being photodegradable, achieves 8 % efficiency (ref. 24).
- [22] Sayama, K.; Mukasa, K.; Abe, R.; Abe, Y.; Arakawa, H. Chem. Commun. 2005, 2416-2417.
- [23] Grätzel, M. Nature 2001, 414, 338-344.
- [24] <http://www.hydrogensolar.com/november24.html>.