

A Titanium Disilicide Derived Semiconducting Catalyst for Water Splitting under Solar Radiation—Reversible Storage of Oxygen and Hydrogen**

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Dedicated to Professor Kurt Schaffner on the occasion of his 75th birthday

Hydrogen and oxygen evolution from water using semiconductors and light is an important issue in the exploitation of solar radiation as a sustainable energy.^[1,2] 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 (i.e. the catalyst is degraded). We present titanium disilicide (TiSi₂) as a prototype for the promising new class of silicide semiconductors,^[9] which have not, to date, been used for water splitting.^[1] These semiconducting materials are inexpensive and abundant. One disadvantage might be their poor stability (in particular of TiSi₂ in water). However, we anticipated that sufficient passivation of TiSi₂ by limited oxide formation might render this project successful.^[10]

The light-absorption characteristics of TiSi₂ are ideal for solar applications: 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 (Figure 1). This behavior is atypical of semiconductors since these materials usually exhibit small band-gap spreads. Determination of the quasi Fermi level of electrons at pH 7 of our catalyst showed values of –0.43 eV and –0.41 eV before and during reaction, respectively;^[11] the latter energy level still fulfils the physical requirement for the reduction of protons to form hydrogen.^[12]

The broad-band water-splitting capacity has been ascertained by experiments run at individual wavelength ranges. For this purpose, Rayonet photoreactors were equipped with

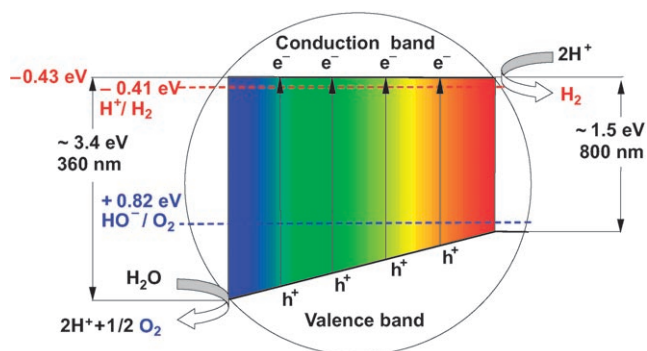
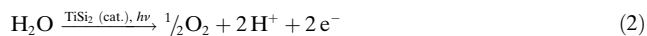
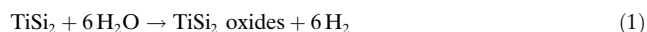


Figure 1. Band-gap range of the TiSi₂-based semiconducting catalyst employed in this work. h⁺ = hole with positive charge.

RUL 350 or 540 nm lamps (λ_{max} ; ± 60 nm emission range). Comparable water-splitting kinetics were obtained.

Two phases (A and B) of hydrogen evolution are observed when dark grey TiSi₂ powder (ca. 325 mesh, Alfa) is allowed to react at 55 °C under standard conditions (see the Experimental Section and Figure 2). Phase A starts at $t=0$ with $[\text{H}_2]=0$ and shows a nonlinear dependence. Phase B is characterized by the nearly linear part of the hydrogen evolution curve. We interpret the time dependence of hydrogen evolution to be a consequence of simultaneously occurring reactions [Eqs. (1)–(3)]. The course of the reaction in



Equation (1), which sacrifices the TiSi₂ by oxide formation, has been verified by runs in the dark at 50–85 °C. Initially, it shows a similar dependence as the reactions in light, but it levels off and does not show a linear dependence as in phase B, which is attributed to water splitting, and hydrogen production comes to a stop after approximately 150 h (Figure 6 in the Supporting Information). The course of hydrogen evolution in phase A depends strongly on the quality and composition of the catalyst, its particle size, the reaction temperature, and the pH value.^[13]

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

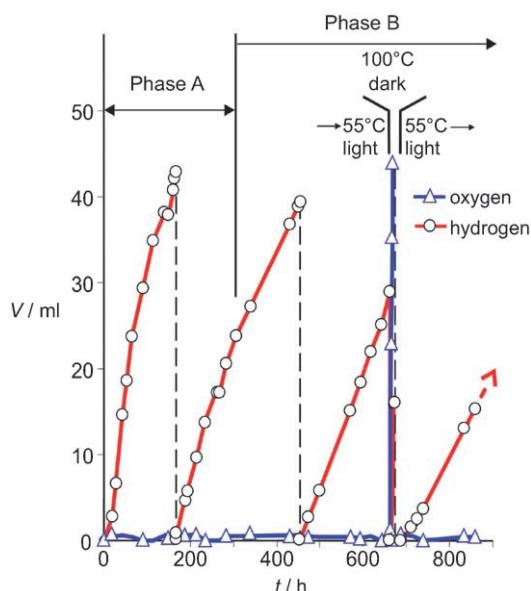


Figure 2. Representative reaction of TiSi_2 (325 mesh) at 55°C under standard conditions. Hydrogen evolution (red) in phase A: formation of the catalytic centers (**cc1** and **cc2** in Figure 3) and start of water oxidation [Reaction (2)] and proton reduction [Reaction (3)] kinetics. -----: nitrogen flush and pressure release (gas concentrations = 0). Phase B (nearly linear kinetics): Over 96% hydrogen evolution from water splitting as judged by comparison with analogous dark reactions. Liberation of dioxygen (blue) from storage upon heating to $\geq 100^\circ\text{C}$ in the dark (run 5 in Table 1); thereafter, irradiation was continued at 55°C .

First convincing evidence that hydrogen production is the result of catalysis was gained by experiments in which hydrogen evolution exceeds stoichiometry that would account for the thermal, noncatalytic, full oxidation of TiSi_2 [Eq. (1)]. That is, over 12 equivalents of dihydrogen are formed in the continuing reactions. Notably, the same argument rules out any type of corrosion, for example, photo-corrosion. Two further pieces of evidence supporting photocatalysis are presented below.

An important experiment concerns the catalytic centers (**cc1** and **cc2**, as referred to in Figure 3). Reactions were run in the dark until hydrogen production ceased; subsequent exposure to light did not lead to further detectable hydrogen evolution (Figure 6 in the Supporting Information). This finding implies that the interaction of light with the catalyst from the onset of the reactions is mandatory for its reactivity for efficient splitting of water. Hence, we may conclude that in phase A of the light-driven reactions, the catalytic centers for water oxidation (**cc1**) and proton reduction (**cc2**) are formed on the surface of the commercially available TiSi_2 . So far we can exclude that these centers are plain TiO_2 , since reactions carried out under the same conditions but with TiO_2 (anatase) as catalyst showed only marginal hydrogen evolution. Further, the reactions are run under inert gas but without degassing the water. Residual dissolved oxygen in water seems to be essential for the reactivity of the catalytic centers, since in completely degassed reaction mixtures the activity of the catalyst is low. On the other hand, in reactions run under

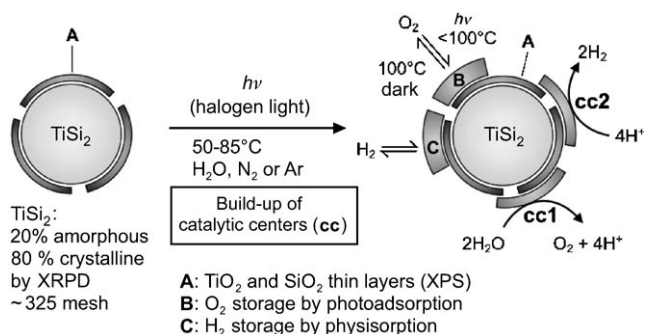


Figure 3. Schematic representation of the proposed in situ formation of the catalytic centers (**cc**) for water oxidation (**cc1**) and proton reduction (**cc2**) within the initial hours of reaction on the surface of commercially available TiSi_2 that is partially covered by thin TiO_2 and SiO_2 layers.

air, reduced activity of the catalyst is also observed. This finding points to a mechanism for the formation of the centers in which limited photooxidation could play a role.

A significant increase in water oxidation and hydrogen formation is found at higher gas pressure (1.1–1.2 bar) while the reaction temperature (50°C) is kept constant (see Figure 7 in the Supporting Information). In an analogous experiment, the temperature was varied (Figure 4), which

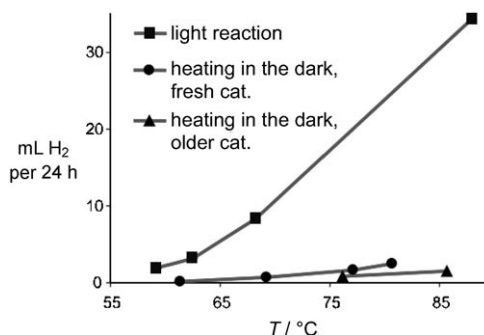


Figure 4. Temperature-dependent efficiency of water splitting as determined by hydrogen evolution.

resulted in higher production efficiencies with increasing temperatures. At 86°C , the production of hydrogen reaches 35 mL per 24 h at 1.1–1.2 bar, which corresponds to a photoenergy conversion η of about 4% for the water splitting process.^[14] We attribute this temperature effect to small but crucial changes of the redox potential of water at elevated temperatures.^[13,16] The efficiency of water splitting achieved with our catalyst compares favorably with those reported for other semiconducting materials used with visible light, all of which have notable drawbacks.^[17] Furthermore, measurements for efficiency calculations that are based on the use of artificial light sources should be evaluated with caution, since most literature values seem to be overestimated.^[18]

Parallel dark reactions (Figure 4), which sacrificially produce hydrogen via Equation (1), rendered at most 4% hydrogen within the higher temperature range. This result

implies that in reactions with light, water splitting accounts for over 96 % of hydrogen evolution. It is especially interesting that, upon aging, the catalyst becomes more stable toward thermal decomposition and produces less hydrogen according to Equation (1), as shown in Figure 4.

A technically valuable aspect of TiSi_2 is its capacity for reversible physical hydrogen storage. Approximately $20 \text{ mL H}_2 \text{ g}^{-1} \text{TiSi}_2$ can be physisorbed at 30°C and $5\text{--}7 \text{ mL H}_2 \text{ g}^{-1} \text{TiSi}_2$ at 50°C . This storage capacity, while lower than those found for other inorganic materials that form metal hydrides, is technically less demanding and requires lower reaction temperatures for desorption of hydrogen.^[19]

In routine runs at temperatures below 100°C , only hydrogen is found in the gas phase, and dioxygen does not appear. Also, hydrogen peroxide is detected in neither the gas nor the liquid phase. In fact, oxygen is efficiently photoadsorbed by the catalyst in light and at any temperature. Conveniently, it is desorbed under very different conditions than hydrogen, thus allowing easy separation of the two gases. Quantitative (within the experimental error of $\pm 15\%$) release of dioxygen sets in rapidly when reaction slurries are heated to $\geq 100^\circ\text{C}$ in the dark (see Figure 2 and the Supporting Information, Figure 7); these and further results are summarized in Table 1. An H_2/O_2 stoichiometric ratio of 2:1 results in phase B of the reactions, while the initial thermal hydrogen evolution in phase A ceases (max. 12–16 mL, see footnote [g] runs 2–5 in Table 1). Notably, this result exemplifies for the first time efficient and controlled desorption of physisorbed dioxygen from a semiconductor surface at a temperature as low as 100°C .^[20a]

Table 1: Gas evolution under standard conditions (in mL) at various reaction times and in separate runs. The gas volumes are given in mL.

Run	H_2 ^[a] a	H_2 ^[b] b = mL $\text{O}_2 \times 2$	H_2 ^[c] c = a – b	O_2 ^[d]
1 ^[e]	6	< 6	< 6	< 3 ^[h,i]
2	24	10	14 ^[g]	5 ^[i]
3	40	24	16 ^[g]	12 ^[i]
4	42	30	12 ^[g]	15 ^[i]
5 ^[f]	112	96	16 ^[g]	48 ^[i]

[a] Total in gas phase. [b] From water splitting according to Equations (2) and (3). [c] Thermal from Equation (1). [d] Evolved from storage. Gas phase plus less than 3 mL dissolved in water. [e] See the Supporting Information, Figure 7. [f] See Figure 2. [g] In these reactions no further measurable thermal hydrogen evolution is found, that is, these values remain constant within an error limit of $\pm 15\%$. [h] Below the detection limit in gas phase. [i] Desorption at $\geq 100^\circ\text{C}$ in the dark.

With this background, it is of interest to compare our results with a recent study of the adsorption of oxygen in the course of its assumed photoreduction at a TiO_2 surface. The study employed ab initio calculations based on infrared data.^[21] In that work, it was concluded that desorption of (ionized) oxygen should be hardly possible from the surface of such a gas–solid system. Another investigation in line with our findings found a high storage capacity of TiO_2 for oxygen (ca. 25 wt %);^[20b] an equilibrium between TiO_2 and a lower oxide is proposed as an oxygen trap in analogy to CeO_2 .^[22] A preliminary determination found an oxygen storage capacity

of more than 15 wt % for our experiments within the temperature range of the standard conditions.^[13]

We favor the idea that in the present reactions with the TiSi_2 -derived catalyst, water-solubilized dioxygen leaves the catalytic centers (**cc1**) after photolytic water oxidation and is photoadsorbed at the original thin-layered TiO_2 sites (2–5 nm thick) at the surface of the catalyst (see XRPD and XP spectroscopy below). In this way, ionic columns of oxygen are formed, which might be held together by charge transfer, and from which O_2 can be released upon thermal activation in the dark.

Water splitting was additionally demonstrated by irradiation under standard conditions but with 10 % H_2^{18}O -enriched water to give fractions of $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ besides $^{16}\text{O}_2$ in the gas phase after desorption, as determined by mass spectrometry. The measurements revealed ^{18}O isotope enrichment in a ratio of $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O} = 43$ (theoretical value: 4.5 for 10 % enrichment) as compared to the theoretical natural ratio of 249 in air (see Figure 8 in the Supporting Information). A more precise result is difficult to reach, because air leakage is hard to avoid.^[13] Moreover, a carbon dioxide signal with varying intensity has been recorded (inset in Figure 8); the origin of the carbon is, however, unclear at present.^[13]

X-ray powder diffraction (XRPD) and X-ray photoelectron spectroscopy (XPS) revealed structural changes of TiSi_2 in water and upon irradiation. The two methods are complementary since XRPD mainly analyzes the crystalline phases of the bulk material, whereas information about the chemical composition of the surface is provided by XPS. An average sample of TiSi_2 shows 80 % crystalline and 20 % amorphous phases as determined by XRPD. The major component of the samples is TiSi_2 . Both composite regions of the TiSi_2 are covered in part by a thin oxide layer, and 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 after sputtering, are limited to a few molecular layers in depth.

The XRPD pattern of a sample which has run for 1000 h at 60°C under standard conditions shows several crystalline phases^[23] (Figure 9 in Supporting Information) and is unchanged as compared to a sample analysis of starting TiSi_2 . Main crystalline components are TiSi_2 , followed by TiSi and metallic Si and Ti. No reflections belonging to SiO_2 or TiO_2 phases are visible.

A different view is given by the XPS data. After removing the oxide layer gradually by sputtering, the contribution of metallic components to the surface is significantly increased. After more than 10 min of sputtering with Ar^+ ions, the ratio of oxidized to metallic species stabilizes. The spectra in Figure 5 represent the Ti 2p photopeaks before sputtering of the sample and after different times of sputtering (Figure 5a) and the corresponding Si 2p peaks (Figure 5b). Both spectra measured before sputtering show that a thin surface layer is highly oxidized. Only small photopeaks belonging to the intermetallic Ti–Si compounds are visible. The pattern reveals no noticeable structural changes of the catalyst even after extended reaction times.

From the XRPD experiments we know that no crystalline oxides are present. On the other hand, the XPS data clearly

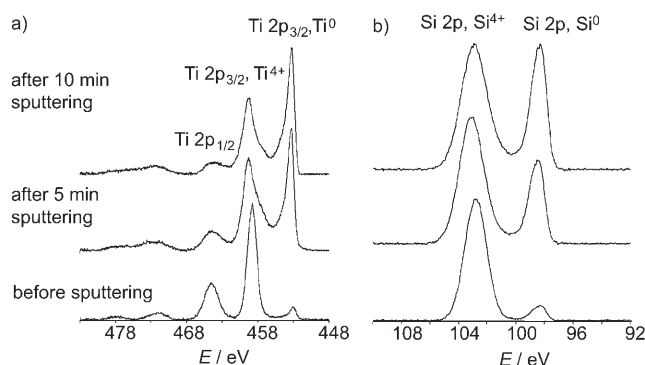


Figure 5. XP spectra before and after sputtering the catalyst with Ar^+ ions.

show that the surface is coated by oxidic species. The fact that these species are “invisible” for XRPD could either mean that the crystallite size of the oxides is smaller than 2–5 nm, that the oxide layer is too thin resulting in too small of a diffraction volume, or that the oxide layer is not crystalline at all. In any event, the oxide layer is not thicker than 2–5 nm. No noticeable change of relative peak intensities is found for “ TiSi_2 ” samples by XRPD and XPS after about 200 h of reaction time. This finding documents that the catalyst has become chemically stable.

In conclusion, we show here for the first time that a semiconducting material such as the inexpensive and abundant TiSi_2 , which is mainly nonoxidic, can serve as a basis for tandem oxidation of water and reduction of protons to form oxygen and hydrogen, respectively, under solar radiation. The catalytically active form of the semiconductor, formed in situ, absorbs a wide range of the solar spectrum.

Catalytic water splitting is documented by the following results (a–c):

- Hydrogen production exceeds stoichiometry that would account for a noncatalytic process such as given in Equation (1),
- hydrogen and oxygen are evolved in a 2:1 ratio, and
- ^{18}O -labeled dioxygen is found in the gas phase during reactions with ^{18}O -enriched water.

The catalytic centers for water oxidation (**cc1**) and hydrogen formation (**cc2**) are formed on the surface of commercially available TiSi_2 in the initial hours of reaction in light and in the presence of a small amount of oxygen. This result could mean that the formation of the catalytic centers involves photooxidation. Harmful oxidation of the silicide is prevented by efficient passivation of its surface by a stable oxide layer of a few nanometers thickness upon reaction in water. Further, a high storage capacity for oxygen is found at temperatures below 100 °C under irradiation; moderate hydrogen storage is observed under these conditions. Desorption of oxygen is achieved at ≥ 100 °C in the dark, which is the lowest temperature applied to date for such a process. This desorption should be highly exothermic and should also deliver energy by volume expansion.

The important result concerning reversible photoadsorption of oxygen at low temperatures allows convenient

separation of the product gases hydrogen and oxygen, which have different physisorption properties. The stability of the TiSi_2 -derived catalyst has been tested over 4–5 months, and a much longer lifetime can be predicted on the basis of the XPS and XRPD data.

Recently, the water splitting reactions discussed above have been successfully tested under concentrated solar radiation.

Experimental Section

Standard conditions: Suspensions of TiSi_2 in either tridistilled or tap water (both give identical results) at pH 7 were irradiated at 50 to 85 °C in round-bottomed and gas-tight stoppered flasks (rubber septum) equipped with a gently stirring magnetic bar. The reactions were generally carried out under nitrogen without degassing the water; a few experiments were run under argon, which gave comparable results. Nitrogen is preferred, however, since it serves conveniently as an internal reference gas for GC analysis. Externally positioned halogen lamps with wavelength emissions closely mimicking solar radiation served as the 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 (thermal conductivity detection; 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 (dashed lines in Figure 2 and in the Supporting Information, Figure 7). The reactions were run with TiSi_2 (2 g, Alfa)^[24] in water (150 mL), ensuring 100% light absorption within 20 cm^2 of aperture and giving rise to optimal storage of oxygen.

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