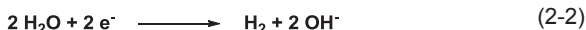
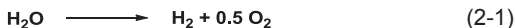


2 Literature Overview

2.1 Water Splitting

2.1.1 Hydrogen from Convenient Water Splitting

Hydrogen is required for several applications. Besides classic chemical use like the Haber-Bosch process, coal liquefaction or for hydrogenation, it is to be considered as an energy carrier.^[1,2] Ever since hydrogen has been used on a large scale, there has been the need for an efficient, cheap hydrogen production.^[3] In the past, numerous ways of hydrogen production were developed. Still, fossil fuels are regarded to be the prerequisite for steam reforming.^[4] Furthermore, partial oxidation or coal gasification are also depending on fossil fuels.^[5] Recently, biomass reforming has become more and more attractive. Obviously, hydrogen and oxygen can be produced by water splitting. While several methods are possible (e.g. thermal decomposition of water or photobiological water splitting), electrolysis is the most common. With around 5 % of the overall hydrogen production it is still a minor issue for industrial application compared to steam reforming.^[6] Nevertheless, photocatalytical water splitting gained attention, because it converts the primary energy light into a chemical energy carrier, e.g. hydrogen.^[7] It is proposed that hydrogen could alternatively be used as an energy-rich reagent for formation of hydrocarbons using atmospheric CO₂.^[2]



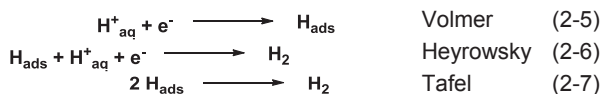
Given that equation (2-1) is clearly an endergonic reaction with $\Delta G = 237 \text{ kJ mol}^{-1} = 1.23 \text{ eV}$. It is a requirement that some sort of energy must be fed to the system. In order to understand the ongoing research in photocatalytical and photoelectrochemical water splitting, the fundamentals of water electrolysis must be understood. While reaction (2-2) is the cathodic reduction and (2-3) is the anodic oxidation of water in alkaline electrolysis, it should be noted that the voltage ΔU to drive an open electrochemical cell is given in equation (2-4). Anyhow, two electrons have to move from the cathode to the anode.

$$\Delta U = \frac{\Delta G}{nF} + IR + \Sigma \eta \quad (2-4)$$

While the number of electrons n , the Faraday constant F and the free Gibbs energy ΔG are set by the reaction itself, the current I , the total ohmic series resistance R and the overpotentials η can be influenced by designing the electrodes or a possible pho-

toelectrical catalyst.^[3] Hence, it has to be considered that oxygen can have an overpotential of about one volt for elemental metals^[8], while the hydrogen overpotential is about half a volt for graphite.^[9] The electrodes must not only be conducting but also have a low overpotential for hydrogen and oxygen. Of course, an increased current is favorable due to a higher reaction rate and can be achieved by a higher contact between electrodes and the liquid. Nevertheless, the ohmic series resistance is supposed to be kept low.

Because the kinetics of hydrogen evolution from water electrolysis and the kinetics of photocatalytic hydrogen evolution from water can supposedly be compared, the mechanism and the kinetic will be discussed in the following.



The equations (2-5) to (2-7) describe the possible mechanisms of electrochemical hydrogen evolution. At first the hydrogen has to be adsorbed and reduced on the solid surface (2-5, Volmer mechanism). The second step depends on the affinity of the electrode towards hydrogen adsorption. For a low affinity equation (2-6) – Heyrowsky mechanism – is favored. For a high affinity equation 2-7 – Tafel mechanism – is preferred. Therefore there are two possibilities of the overall proton reduction: Volmer-Tafel and Volmer-Heyrowski. For metals, the Volmer mechanism is most commonly the rate determining step. It is not surprising that metals with a medium metal-hydrogen bond energy inhibit neither Hyrowsky-mechanism nor the Tafel-mechanism.^[10] Platinum, palladium and other noble metals are known to have low electrode overpotential. Thus, they have a medium metal-hydrogen bond energy, which leads to a fast Volmer-mechanism reaction, resulting in a quick reaction at rate determining step.

Electrolysis of water or photocatalytic water splitting is always a zero-order reaction. A zero-rate reaction is found, when the reaction rate is independent on the concentration of the reactants. This is the case for reactions, when the reaction rate depends on catalysts saturated with reactants. The reaction rate r_A is constant over time t , because the increase or decrease of the concentration dc_A is constant; giving a system that depends only in the reaction rate coefficient k_A (equation 2-8). Since the diffusion to the surface is faster than the rate determining Volmer reaction, the concentration of the adsorbed H_{ads} will remain constant over the reaction time. This is the case for water splitting depending only on the surface of the catalyst and the applied bias. By altering the latter variable, k_A can be changed, but not the reaction order. Of course, photocatalytic reactions are special, because they occur mostly only under irradiation.

While changing from electrolysis of water to photocatalytic water splitting, the origin of the bias changes instead of the reaction order.

$$r_A = \frac{dc_A}{t} = k_A \quad (2-8)$$

2.1.2 Photocatalytic Water Splitting and Hydrogen Evolution from Water

In general, photocatalysis can be divided in three groups. The excitement or stabilization of a reactant leads to a catalytic reaction what is characteristic for catalytic photo-reactions. The reaction would not occur without light or catalyst. In photosensitized and photoassisted catalytic reactions the catalyst itself is required to be excited. For photosensitizing just an initial irradiation is required, after which the reaction will proceed even in the dark. Photoswitches are a typical example for this reaction type. Photoassisted reactions require a permanent irradiation of the catalyst, because the received light energy of the catalyst is transferred to the reactant during the reaction. The provided energy is a prerequisite for the reaction of the reactant or reactants. Therefore, photocatalytic water splitting or hydrogen evolution from water can be described as photoassisted catalysis.^[11]

While various methods for water splitting from light are imaginable and applicable, photoelectrosynthetic cells (PECs) and suspended photocatalysts are the most encouraging challenges.^[12] The energy conversion efficiency from sunlight to hydrogen is low. Still, 16 % efficiency of a commercial available photovoltaic cell plus electrolysis would exceed 12 % efficiency of the best PECs in laboratory scale.^[13] Photocatalytic water splitting or photocatalytic electrolysis of water was discovered by *Fujishima* and *Honda*.^[14,15] They established illuminated TiO₂ as the material for “artificial photosynthesis”. Though, in these experiments TiO₂ was used as the photoanode, while platinum was used as the metal cathode, it was postulated, that colloid systems would also split water.^[16,17] Nevertheless, a first commercial attempt of using titania for solar energy conversion was done by *Grätzel*: a combination of nanocrystalline TiO₂ and certain dyes supported on a transparent conducting oxide as anode.^[18]

As described in section 2.1.1, water can be split by electrical current. Photocatalytic water splitting is achieved by a photogenerated electron and an electron hole within a semiconductor. While the potential of an excited electron, which was promoted to the conduction band, has to be lower than 0.00 V, the remaining hole in the valence band must have a potential above 1.23 V in order to split water into its elements. The band edge energies must straddle the electrochemical potentials of E°(H⁺/H₂) and E°(O₂/H₂O) to drive the hydrogen or oxygen evolution reaction, respectively. This is illustrated in Figure 2-1a.^[19] Thus, in terms of thermodynamics photocatalytic water splitting is not very extraordinary. Since the free enthalpy of the reaction is 1.23 eV, a semiconductor material is needed whose absorption edge is above that energy.

Hence, the wavelength of light used for water splitting is required to be less than 1010 nm. Though this would cover the whole visible and a part of the near infrared spectrum, the overpotential for the oxidation and reduction of water inhibits photoelectrolysis for the most semiconductors. This is observed, even if an appropriate catalyst is used for the generation of electron-hole pairs. Therefore, the required band gap of a semiconductor for water splitting is reported to be between 1.6 eV and 2.4 eV.^[20] Anyhow, working photochemical electrodes can be designed in two configurations: Schottky type cells have a photoanode-cathode configuration and Tandem or Z-Scheme type cells use a photoanode-photocathode configuration. The latter have the advantage of two smaller band gaps instead of a single, large one. Thus, a greater fraction of the solar spectrum can be used.^[12] Though, when it comes down to use suspended photocatalysts, just Schottky type cells seem to have reasonable efficiency.^[21,22] This might be because of the difficult synthesis of two microscale semiconductor particles, which have an ohmic contact.

After the demonstration of *Fujishima* and *Honda* of artificial photosynthesis, photocatalytic effects were demonstrated on suspended semiconductor particles.^[14] Furthermore, it was assumed that the basic functions of a "photoelectrosynthetic" cell could be imitated by nano- or microscale objects. Light absorption, charge separation and water electrolysis is supposed to be accomplished by one particle instead of two electrodes. The principle is illustrated in Figure 2-1b.^[23] There were early attempts with colloid TiO₂ structures which showed no overall water splitting. As it is depicted, after the generation of an electron-hole pair, the migration to the surface is a prerequisite for the catalytic reaction. Crystal structure, crystallinity and particle size can clearly influence migration. Crystal defects may affect the lifetime of an electron-hole pair, since they can recombine at these centers. In smaller particles the way to the reaction sites becomes shorter, which leads to a decreased probability for electron-hole recombination.

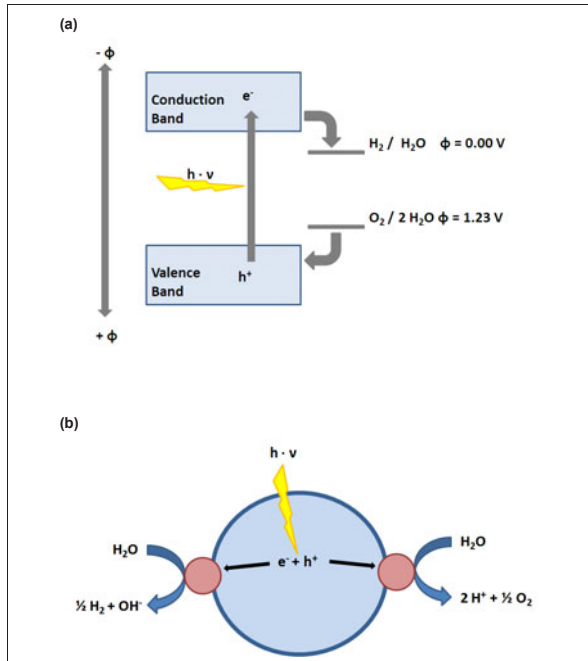


Figure 2-1: Principles of photoelectrolysis of water. (a) Schematic illustration of the band gap prerequisite of semiconductor for water splitting. (b) Model for the charge separation by irradiation within the photocatalyst and hydrogen plus oxygen evolution by deposited promoters.

Furthermore, the reactive surface character and the number of active sites are important. It was repeatedly reported, that sufficient photocatalytic water splitting was observed only in the presence of deposited nanocomposites for some semiconductors catalyzing the oxygen evolution reaction, the hydrogen evolution reaction or both. Although for the most metal oxide a promoter is not needed for oxygen production, still, hydrogen evolution is depending on typical promoter for hydrogen reactions like Pt, Pd or Rh.^[7,19] Considerations of the nanostructuring of catalyst and promoters can be found in section 2.1.3.

Although a suitable band and its position are the requirement for photoelectrolysis of water, the energetics of semiconductor liquid interface under irradiation are crucial for the understanding of that process. The actual free energy, which is basically the Fermi energy of the semiconductor, is influenced by the kinetics of the charge carriers under irradiation. Therefore the effective band gap under illumination is smaller than in the dark. Hence, water cannot be split by a catalyst under irradiation unless the photovoltage is less than 1.23 V.^[24] Kinetically, the formation rate of charge carriers must be higher than their consumption rate. Therefore, five non-positively contributing effi-

ciency processes can be outlined. These are illustrated in Figure 2-2. The photogenerated electron-hole pair is able to recombine in the bulk (1), in the depletion region (2) or at surface defects (3). Furthermore, electrons are able to tunnel through the electric barrier near the surface (4) and escape through thermionic emission.^[12] Thus, it should be the aim developing well organized semiconductors for inhibiting the processes (2) to (5).^[25]

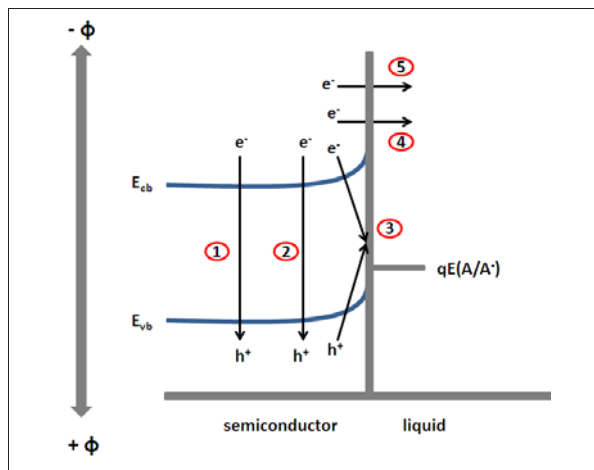


Figure 2-2: Schematic illustration of the recombination pathways of photogenerated electron-hole pairs within a semiconductor under irradiation. The semiconductor is in contact with a liquid and $qE(A/A^-)$ marks the electrochemical potential for the redox couple of acceptor A and donor A⁻.

Semiconductors with insufficient water splitting abilities might be able to split water with a chemical bias such as sacrificial agents being electron donors or acceptors. Hence, hydrogen or oxygen evolution rates are enhanced depending on the nature of the sacrificial agent. On the one hand oxidizing agents like Ag^+ or Fe^{3+} were able to increase the oxygen evolution rate while hydrogen production was suppressed; on the other hand alcohols or thiols achieved the opposite. Sacrificial agents or chemical biases, as they are also referred, are crucial nowadays for sufficient photocatalytic hydrogen evolution from water. This is a huge drawback of this method. Without these agents the hydrogen evolution rate of photocatalyzed water splitting is always close to zero. There were very rare examples of overall water splitting into hydrogen and oxygen. Still, it will be one of the major challenges in the next decades to overcome this problem. Most commonly methanol or triethanolamine is used to get oxidized instead of the oxygen within the water. The lower redox potential of the organic sacrificial agents was discussed to be the major influence for the enhancement of the photo-

catalytic activity. Also the high overpotentials for oxygen oxidation might have a large effect on a suppressed hydrogen evolution.^[26]



Besides all development in photocatalysis, photocorrosion is still the biggest disadvantage of using light as a primary energy source. For example, CdS has been studied for a while and it has a suitable band gap and band gap position, but instead of oxidizing water, the catalyst itself is oxidized without a matching sacrificial agent.^[27] The reaction shown in equation (2-9) can replace O^{2-} oxidation shown in equation (2-3). Although the degree of photocorrosion depending on the used material, it will remain certainly as the main drawback in all kinds of photocatalysis, homogeneously or heterogeneously.

Because nowadays it is state of the art to develop suspended photocatalysts for hydrogen evolution from water, the discussion have to outline the advantages of nanostructured catalysts. Since it became clear that nanostructuring is a prerequisite for the conceptual transition from photoelectrochemical cells to suspended photocatalyst, this quantum effect was used and examined.^[28] This will delineated in section 2.1.3. Nevertheless, even early researches focused on titania nanoparticle photoanodes.

2.1.3 Nanostructuring in Photocatalysis for Sufficient Hydrogen Evolution

Since the groundbreaking talk of physicist Richard Feynman "There is Plenty of Room at the Bottom" in 1956,^[29] nano-technology has had a huge impact on industrial, biomedical, electronic and catalytic applications. This is to take advantage of their small size, resulting in higher specific surface area and properties that are not observed in bulk material like changes of the band gap or ion conductivity. Nanoparticles (NPs) are defined by IUPAC to have dimensions between 1 and 100 nm. NPs can be synthesized by "top down" strategies using vapor deposition etc. or "bottom up" approaches, utilizing classically chemical strategies.^[30,31]



Soft template design became most common for metallic nanoparticles. Therefore, "wet chemical" reduction has proven to be a good method for the preparation of solvent dispersed NPs.^[32] As shown in equation (2-10), the general procedure is straight forward. A metal salt M^{n+} is dissolved with a stabilizer R_{stable} and a reducing agent herein implied as a solved electron e^- . For the reduction of metal salts, several com-

pounds were found to be suitable like hydrogen, borohydrides, alcohols or hydrazines. While the metal is reduced, the stabilizer inhibits growth of the metal nucleus above a certain size and promotes a colloid solubility of the metal cluster.^[30] Additionally, the size of the NPs can be controlled.^[33]

However, the usage of metal NPs for catalysis has been investigated thoroughly. Since the reaction rate for most typical metal catalyzed reaction increases due to a larger specific surface area, there were also investigations about shape- and size-depending effects for these reactions when using catalytically active nanoparticles. There are cases for metallic systems in which the activity goes up or descends with smaller NPs while the surface area is held constant. These effects are called negative or positive size effects. Nevertheless, there are cases in which the activity goes through a maximum of a certain NP core diameter.^[34]

Since there were concepts to apply nanoscaled particles on sufficient water splitting, a lot of research was conducted to improve the catalytic activity of suspended nanoparticles. Nowadays, it is proven that only nanostructured photocatalyst can provide a sufficient hydrogen evolution rate from water when a suspended catalyst is used instead of a photoelectrochemical cell.^[35] The ability of suspended semiconductors to split water is based on the quantum size effect what was already denoted in Figure 2-1 b. Size and electronic properties play an important role. In a solid bulk catalyst is no electron-hole pair separation possible. The pure volume and defect sites of the semiconductor material do not allow the electrons or the positively charged holes to diffuse to the solid surface without recombination.

Though it seems to be obvious that catalytic activity for photocatalytic water splitting can be enhanced by smaller particles due to a higher specific surface area, pros and cons of nanostructures have to be discussed. The following discussion focuses mainly on kinetic aspects regarding light distribution and electron diffusion.^[19]

For water splitting, photoexcited charge carriers are supposed to diffuse to the surface. Because their lifetime is in the range of microseconds, a nanostructured surface or a small NP increases the probability of these electronic states to reach the semiconductor surface. Similar considerations might be done for the light distribution. The degree of horizontal light distribution will be enlarged by light scattering. In general, this effect can clearly be seen by UV/Vis absorption measurements of colloidal suspensions. Certainly, quantum size confinement is most important regarding photocatalytic experiments using a semiconductor. *Holmes et al.* observed a logarithmic size-dependency in catalysis using CdSe quantum dots.^[36] That can be explained by a growing band gap when the size of the particle decreases. Derived from the Marcus-Gerischer theory increasing thermodynamic driving force accelerates the reaction for electrolysis.^[37] All these effects have been applied to photoelectrolysis. Besides all positive effects, there are negative contributions from NPs for photocatalysis. As im-

plied in Figure 2-2, a higher specific surface area allows a higher surface electron recombination rate. Hence, the quantum efficiency decreases. Intuitively, in smaller particles the space for charge carrier separation is reduced. The charge layers are not effectively isolated and additional energy would be required.

However, two major disadvantages of nanostructuring are a lower photon flux at surfaces leading to a lower flux to specific surface area ratio and a slow interparticle charge transport due to carrier diffusion instead of carrier drift. All the pros and cons will have to be considered to outline a good strategy for heterogeneous photocatalysis.^[19]

Although early results of *Grätzel* neglected a satisfactory water splitting reaction, recently, microscaled suspended photocatalysts worked under ultraviolet conditions without a chemical bias. Nevertheless, all of them are Schottky type devices, but only a few compounds showed overall water splitting.

There were inter alia transition metal compounds like RuO₂ modified LiNbO₃.^[38] Water splitting is complex, kinetically slower, more corrosive and highly endergonic compared to a single-electron-transfer. Fe₂O₃, WO₃ or MnO₂ have been developed as nanostructured photoelectrodes which might be used for a bias-free photoelectrolysis.^[39] These materials were improved with small promoters like NiO, IrO₂ or MoS₂. The latest research focuses on several techniques and materials, in order to tailor the properties and the catalytic activity. As already mentioned, it is the overall aim to develop nanostructured photocatalyst in suspension. Most common are metal oxides in general. ZnO, TiO₂ and Fe₂O₃ are very promising, because they have a suitable band gap for water splitting. Although cobalt modifications of these materials were performed to enhance the photocurrent, they lack in catalytic activity towards water splitting experiment.^[16,40] The performance is better with materials containing niobates, which would be expensive in a large scale. Furthermore, nickel and tantalum catalyst showed recently a reasonable activity.^[41] Still, photocorrosion, the difficult synthesis and the costs of these systems will remain a major drawback of metal oxides. Unfortunately, the most common semiconductors with a suitable band gap are metal chalcogenides which underlie the same processes as the described photocatalysts. Recently, graphitic carbon nitride was discovered as a photocatalytic active semiconductor for hydrogen evolution, which has shown none of the disadvantages so far.

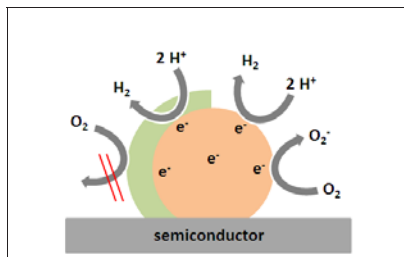


Figure 2-3: Illustration of the effect of a Cr_2O_3 shell surrounding a noble metal cocatalyst on an illuminated semiconductor-photocatalyst.

The benefit of promoters for electrode reactions have been known for 40 years.^[42] More specifically, electron injection from TiO_2 into gold NPs and hole injection into RuO_2 was directly observed by transient absorption spectroscopy.^[43] Furthermore, Pd, Ru, Rh and Pt are well studied for their properties as cocatalysts for water reduction reactions.^[22] For photocatalytic water splitting, the reaction rate becomes equal to the rate of the back reaction at certain H_2 and O_2 concentrations. Therefore, *Domen et al.* elucidated that a 2 nm layer of Cr_2O_3 on the cocatalyst catalyzes a proton reduction but inhibits reduction of the generated oxygen. That is illustrated in Figure 2-3.^[44] Nevertheless, there have been also reports about several oxides promoting the oxidation at photoactive semiconductors like IrO_2 or different cobalt oxides. This might be attributed to the reduction of the overpotential.^[45] Investigations on promoters for photocatalytic hydrogen evolution from water will be crucial for the development and success of that method.

2.2 Graphitic Carbon Nitrides

2.2.1 Structure

The history of graphitic carbon nitrides reaches back to *Liebig* who discovered the so called “melon”.^[46] Until 1990, this class of compounds was not attractive for research.^[47] It was the theoretical prediction of β -carbon nitride which led to experimental activities.^[48] Nowadays, there are many efforts toward synthesis and characterization of graphitic carbon nitrides.^[49] In general, graphitic carbon nitrides, a class of materials with a carbon nitrogen ratio close to three to four, are often referred as g- C_3N_4 . Although there have been many attempts, this compound could not be crystallized well enough for X-ray crystal analysis.^[50,51] It is said, that nanostructuring, template chemistry and copolymeric modification are supposed to be more important for material design than growing of single crystals. In 2006, this class of materials was considered to be used in metal-free catalysis.^[52]

Modified Graphitic Carbon Nitrides for Photocatalytic
Hydrogen Evolution from Water

Copolymers, Sensitizers and Nanoparticles

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