



50 Years of Materials Research for Photocatalytic Water Splitting

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50 years ago, Fujishima and Honda published their work on photoelectrocatalytic water splitting with the aid of the light absorbing semiconductor TiO₂. Since then, many different novel absorber materials for water splitting have been discovered and

investigated. This Minireview aims to briefly summarize the most important materials developments for photocatalytic water splitting of that time, differentiating between single absorbers and Z-schemes.

1. Introduction

One of the most pressing challenges of our society today is the replacement of conventional carbon-based fossil fuels with alternative energy carriers that do not contribute to climate change. In the revised Renewable Energy Directive the overall EU target for the consumption of renewable energy sources by 2030 was raised to 32%.^[1] To reach this goal and beyond, the need of efficient and alternative green energy carriers is imminent.

The most straightforward path to renewable fuels is by employing photovoltaic or wind energy for the splitting of water into oxygen and hydrogen, storing renewable energy for times of low light intensity or little wind in the chemical bonds of the products. Produced this way, hydrogen is a green energy carrier and burning fuel whose generation or burning does not produce carbon dioxide. Today, photovoltaic cells coupled to water electrolyzers have the best efficiency for the water splitting reaction, but the high cost of this technology is an obstacle to the global scale up that is required to match the world's needs.

An alternative way to convert solar energy into hydrogen is to perform water splitting at the surface of semiconductors. In 1971, 50 years ago, Fujishima and Honda published their results on utilizing for the first time a light-irradiated semiconductor material for water splitting.^[2] A TiO₂ photoelectrode was used for light absorption, which resulted in photoelectrochemical overall water splitting.^[3]

Photocatalytic water splitting is possible by heterogeneous photocatalysis.^[4] In heterogeneous photocatalysis, semiconductor materials are irradiated with light. When the energy of the incoming light is higher than the band gap of the irradiated

semiconductor, charge carriers are generated inside the semiconductor absorber material by excitation of electrons from the valence band (VB) into the conduction band (CB) using absorbed light energy. After charge separation, the photo-generated charge carriers have to travel through the absorber to the surface for the subsequent surface reaction, the irradiated photons can be considered as educts of the overall reaction.

The excited charge carriers in the semiconductor, electrons in the CB and defect electrons (holes) in the VB, diffuse to the surface of the semiconductor where they can undergo redox reactions with available electron donors (D) and electron acceptors (A). Protons in water can e.g. be reduced by photoexcited electrons to form H₂. As the counter oxidation, water can be oxidised to oxygen, as such the overall reaction is photocatalytic water splitting.

There is however ongoing misuse of the term water splitting, as was recently also critically discussed elsewhere.^[5] Still, in many studies using sacrificial alcohols for the hole oxidation reaction the wording "water splitting" is used, which is not correct. The same is also valid when electron scavengers are used, however it seems that hydrogen generation and water splitting are more often used incorrectly. The term water splitting should only be used when pure water is used as solvent and reactant, without any additional reagents like alcohols.

Photocatalytic water splitting is thermodynamically a photosynthetic reaction,^[6] since the overall water splitting reaction (H₂O → H₂ + 1/2 O₂) is an uphill reaction, with a large positive shift in Gibbs free energy (+237 kJ/mol). For charge accumulation of 2 or 4 charges, respectively, co-catalysts for the half reactions (oxidation of water to oxygen and protons, reduction of protons to hydrogen) are mostly needed for water splitting to take place. Thus, solar light is actually stored in the chemical bonds of hydrogen and oxygen. Moreover, the back reaction to water, which can take place on the same co-catalysts catalysing the photosynthetic reaction, has to be inhibited, since it is the thermodynamically more favoured reaction.

The main problem of this photocatalytic mechanism is that photogenerated charge carriers can recombine on their pathway to the surface. Recombination describes the scattering of photoexcited electrons at grain boundaries and defects inside a

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Part of the joint "German Chemical Society ADUC Prizewinner" Collection with EurJOC.

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semiconductor material, falling back to the VB and losing all potential energy from light absorption. In addition to bulk defects, surface defects like vacant atom positions act as recombination sites, too. Therefore, the intermediates of the heterogeneous photocatalysis reaction, the photogenerated charge carriers, can already be lost before reaching the reaction sites at the surface. This makes the inhibition of charge carrier recombination the most important task and challenge to improve photocatalytic efficiencies.

Since 1972, many different semiconductor materials for photocatalytic water splitting have been investigated, but many of them do not absorb enough visible light for a viable scale-up.^[4,7–9] In recent years, several new semiconductor materials have been discovered for solar water splitting in visible light.^[10] This Minireview wants to give a short historical overview of materials development in the field, leading to more recent results including immobilization of particle suspensions. It concentrates on single absorber materials and Z-schemes, for which the most recent promising progress has been reported.

2. Single absorber materials

TiO₂ was first used as a photoelectrode for photoelectrochemical water splitting. Later, it was investigated also in powder form for photocatalytic water splitting. However, sole TiO₂ cannot split water or generate hydrogen photocatalytically without any modification, like noble metal decoration^[11] or formation of a heterojunction. Treatment with sodium hydroxide^[12] or alkali carbonates^[12] of such noble metal decorated TiO₂ was reported to perform photocatalytic water splitting in UV light, the latter reducing the back reaction due to carbonate surface coverage.

In the 1980s and 1990s, a vast number of new metal oxide photocatalysts active for water splitting have been discovered and reported, especially in Japan. Usually they are classified into two classes, materials containing metal cations with d^0 (Ti⁴⁺,

Zr⁴⁺, Ta⁵⁺, Nb⁵⁺, W⁶⁺) or d^{10} (Ga³⁺, In³⁺, Ge⁴⁺, Sn⁴⁺, Sb⁵⁺) electron configuration. Binary, ternary and quaternary semiconductor oxides were prepared by different synthesis techniques, mainly solid state reactions fusing different metal oxides to more complex compounds. Very good overviews on all such materials are given in excellent review articles.^[8,13,14]

One of the most investigated oxide semiconductors for photocatalytic water splitting with d^0 configuration is NaTaO₃, first reported 1998 for this reaction.^[15] By decorating it with NiO and doping with La, a record water splitting quantum efficiency of 56% at 270 nm was achieved.^[16] Until today, the origin of its exceptionally high activity is utilized in literature,^[17,18] and a vast number of different dopants has been investigated into NaTaO₃ including e.g. Sr.^[19,20]

Another early metal oxide that has recently experienced a tremendous renaissance is SrTiO₃. It was first reported for overall water splitting in 1980, when decorated with NiO.^[21] Since then, many studies have been performed to improve its performance. In 2004, Kudo et al. doped SrTiO₃ with different metal cations, upon which SrTiO₃ became able to absorb visible light. Rh-doped SrTiO₃ is, since then, one of the most used photocatalysts for hydrogen generation, and one of the most used hydrogen evolution photocatalysts when combined with other oxygen evolution photocatalysts in Z-scheme systems.^[22] In 2016, La/Rh-doped SrTiO₃ was combined with Mo-doped BiVO₄ for the best known powder-based oxide photocatalyst for water splitting, a Z-scheme in the shape of an immobilised photocatalysts sheet, with Au as electron mediator, that could turn sunlight into hydrogen fuel with solar-to-hydrogen efficiency of 1.1%.^[23]

As a single absorber material for photocatalytic water splitting, aliovalent doping for defect engineering was reported in 2009 to reduce the intrinsic defects of SrTiO₃ by La or Ga doping.^[24] In 2016, Al doping turned out to enhance the quantum efficiency of SrTiO₃ for water splitting dramatically, up to 30% at 360 nm. Later, this efficiency was enhanced to 56% quantum efficiency at 365 nm (Figure 1).^[25]

Since then, further studies on this enhancement have been reported, including investigations on the amount of Al,^[26] long time stability,^[27] and alternative dopants.^[28] In 2020, an external quantum efficiency of 95.9% at 360 nm could be reported, this further improvement could be achieved by site-specific cocatalyst decoration onto the Al-doped SrTiO₃ particles with Rh/Cr₂O₃ and CoOOH.^[29]

Ga₂O₃ is a very active oxide with d^{10} configuration for photocatalytic water splitting in UV light when decorated with NiO,^[30] but especially when doped with Zn.^[31] However, as most of the examples above, only UV light, which only contributes to small amounts to solar light irradiation, can be utilized for charge carrier generation, in the case of Ga₂O₃ UV-C light is necessary. Many more oxide photocatalysts with d^{10} configuration for water splitting under UV irradiation have been reported, none reaching the activity of Ga₂O₃:Zn.^[13]

By mixing Ga₂O₃ and ZnO and treating it in ammonia gas, Maeda and Domen reported in 2005 the first visible light absorbing solid solution GaN:ZnO which was able to split water photocatalytically into stoichiometric amounts of hydrogen and



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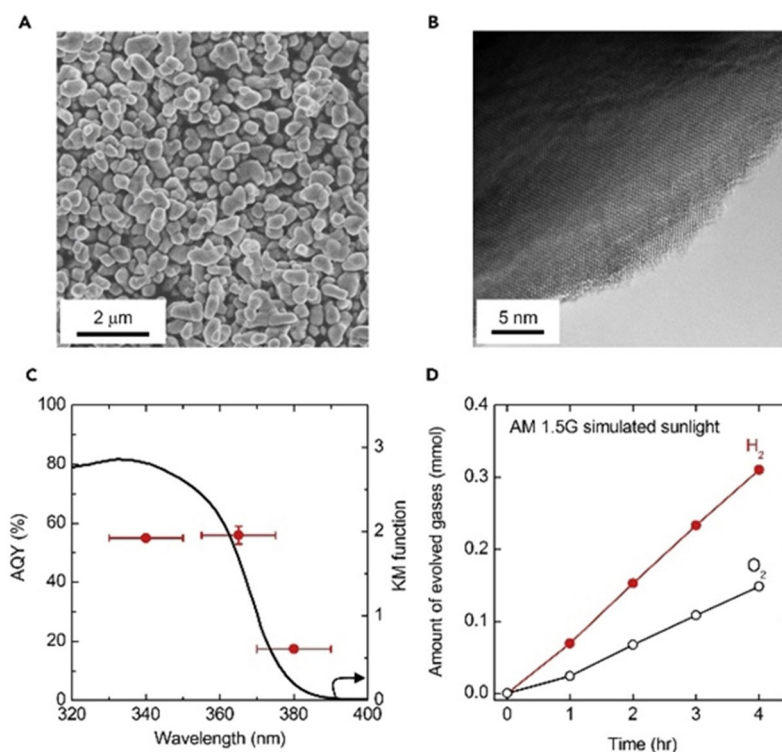


Figure 1. A) SEM image of SrTiO₃:Al; B) HR-TEM image of RhCrO_x/SrTiO₃:Al; C) Apparent quantum yield (AQY) of SrTiO₃:Al plotted as a function of wavelength of the incident light. The black solid line represents the diffuse reflectance spectrum of SrTiO₃:Al under simulated sunlight (AM 1.5G) using cocatalyst RhCrO_x (Rh 0.1 wt%, Cr 0.1 wt%). The reaction was carried out at 288 K and 10 kPa. Reprinted from ref.,[25] Copyright (2018), with permission from Elsevier.

oxygen, after co-catalyst decoration with Rh/Cr₂O₃ core-shell cocatalyst.^[32–37] This co-catalyst gained special attention, since it was identified at that time to be responsible to inhibit the back reaction of hydrogen and oxygen to water, therefore leading to stoichiometric water splitting in visible light.^[35] In 2008, photodeposition or impregnation of the mixed metal oxide of Rh and Cr (Rh_{2-y}Cr_yO₃) was shown to have the same co-catalyst effect when decorating (Ga_{1-x}Zn_x)(N_{1-x}O_x).^[38,39] In the same way, also Zn_{1.44}GeN_{2.08}O_{0.38} decorated with RuO₂ was reported for overall water splitting,^[40] and photodeposition of Rh_{2-y}Cr_yO₃ also resulted in water splitting activity.^[38] Recently, AgTaO₃ was decorated with a similar co-catalyst with defined stoichiometry, Rh_{0.5}Cr_{1.5}O₃, resulting in overall water splitting with an apparent quantum yield of 40% at 340 nm and a solar-to-hydrogen efficiency of 0.13%.^[41]

Searching for visible light absorbing materials, TiO₂ played an important role in materials research. A very prominent strategy in the early 2000s was non-metal doping of stable and well-known oxides,^[42] including TiO₂, with e.g. nitrogen and/or sulfur anions. In 2006, Kisch determined the origin of visible light activity of TiO₂ after treatment with urea, being surface sensitization with melamine condensation products^[43] like “Melon”, a carbon nitride material first reported by Berzelius and Liebig.^[44]

Antonietti et al. described the optical properties, the electronic structure and the photocatalytic activity of layered carbon nitride (g-C₃N₄) photocatalysts in detail in 2009,^[45,46,47]

since then the material has been investigated by many research groups all over the world in attempts to optimize its optical, electronic and catalytic properties.^[48] Interesting and important features of carbon nitride include its relatively low band gap (2.7 eV) and its high VB and CB positions (+1.4 V and -1.3 V at pH 7 vs. normal hydrogen electrode (NHE), respectively) compared to those of many oxide semiconductors.^[49] Thus, it should be able to split water. In 2016, overall water splitting with g-C₃N₄ was reported, utilizing the strategy of dual cocatalysts decoration with Pt, PtO_x, and CoO_x as redox cocatalysts.^[50] The apparent quantum yield (AQY) for the overall water splitting reaction was calculated to be 0.3% at 405 nm.

Many more visible light absorbing single absorber materials for photocatalysis have been reported in the last 30 years, however many of them have no suitable band positions for water splitting (e.g. Fe₂O₃, WO₃, BiVO₄), are prone to photocorrosion (e.g. CdS, GaAs), or do not produce hydrogen and oxygen (e.g. BaTaO₂N) simultaneously.

Oxynitrides are a family of materials that has gained a lot of attention due to their tuneable absorption down to 650 nm.^[51] However, very few oxynitride materials are able to split water. One of them is TaON, whose water splitting activity under visible light irradiation was reported in 2013 by Maeda et al. (Figure 2).^[52] For overall water splitting, it has to be modified with ZrO₂ nanoparticles: ZrO₂/Ta₂O₅ composites are nitrified in ammonia gas to prepare the photocatalyst, and the ZrO₂ seems to prevent Ta⁵⁺ cations at the TaON surface from being reduced

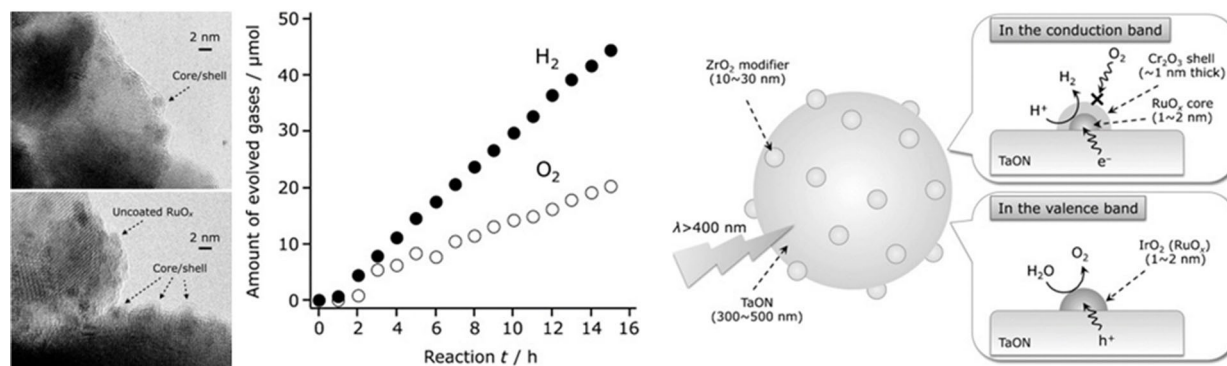


Figure 2. left: HRTEM images of RuO₂/ZrO₂/TaON after Cr₂O₃ photodeposition; middle: water splitting under visible light ($\lambda > 400$ nm) using IrO₂/Cr₂O₃/RuO₂/ZrO₂/TaON; right: Schematic illustration of the mechanism of overall water splitting on IrO₂/Cr₂O₃/RuO₂/ZrO₂/TaON photocatalyst; Reproduced from ref.[52]

during oxynitride formation. The prevention of such surface defects in the reducing atmosphere during nitridation results in stoichiometric water splitting after co-catalyst decoration.

Although many oxynitrides absorb large portions of sunlight, very few can utilize the absorbed light. A few years ago, an oxynitride was reported that was able to utilize most of its absorbed photons up to 600 nm. The complex oxynitride LaMg_xTa_{1-x}O_{1+3x}N_{2-3x} ($x \geq 1/3$) showed water splitting activity after RhCrO_y decoration and additional protection with amorphous thin SiO_x and TiO_x protection layers.^[53] By investigating the influence of lattice composition, another complex water splitting oxynitride was reported, namely LaSc_xTa_{1-x}O_{1+2x}N_{2-2x} ($x \geq 0.5$).^[54]

A comparable TiO_x coating was also used onto CaTaO₂N for photocatalytic water splitting in visible light up to 500 nm.^[55] Photocatalytic water splitting with other earth-alkali analogues, whose band gaps diminish from Ca over Sr to Ba, are not reported yet. However, perovskite oxynitride solid solutions of LaTaON₂ and CaTaO₂N have been recently reported to show enhanced charge carrier separation, leading to overall water splitting in visible light with RhCrO_x-decorated La_{0.1}Ca_{0.9}TaO_{1+y}N_{2-y}.^[56]

Comparable to nitrogen incorporation into oxides, sulphur incorporation to form oxysulphides shifts the valence band edges to more negative values compared to the initial oxides. Compared to sulphides, the mixing of O 2p and S 3p orbitals stabilized the materials towards self oxidation, as known for CdS. However, many oxysulphides do not exhibit enough overpotential for the water oxidation half reaction.^[57] In 2019 the first oxysulfide able to perform photocatalytic overall water splitting was reported.^[58] Cr₂O₃/Rh/IrO₂-loaded Y₂Ti₂O₅S₂ synthesized at 973 K generated hydrogen and oxygen under visible light with an AQE of 0.36 % at 420 nm.

3. Z-scheme water splitting

Many single absorber materials with band gaps in the visible light region have unsuitable band positions for overall water splitting,^[10,13] or do only show activity for one half reaction.^[59]

Therefore, two of them can be combined in Z-schemes to enable overall water splitting.^[22,60] Compared to heterojunctions of two semiconductors,^[61] the flow of charge carriers is reversed in Z-schemes. Recently moreover, Sun et al. showed that Z-schemes or heterojunctions can be consciously constructed.^[62,63]

Until 2013, only 25 material combinations were known as Z-schemes for water splitting, since then many more have been reported for water splitting and CO₂ reduction.

WO₃ and SrTiO₃:Rh are probably the most often used materials for oxygen and hydrogen evolution, respectively, in Z-scheme water splitting systems. Moreover, BiVO₄ has become a highly often used absorber for the oxygen side. Its combination with SrTiO₃:Rh was reported for water splitting already in 2014.^[64] SrTiO₃:Rh was also combined with Ta/N-doped TiO₂,^[65] Fe–H–Cs–WO₃,^[66] Bi₄NbO₈Cl,^[59] and In–Fe(25 %) oxide^[67] for Z-scheme overall water splitting. La doping into SrTiO₃:Rh was shown to improve the hydrogen production rate, when combined with Ta₃N₅.^[68]

Typically, redox couples in solution like Fe²⁺/Fe³⁺ or IO₃⁻/I⁻ are used as mediators, to be reduced by photogenerated electrons from the oxygen-evolving photocatalyst, and to be oxidised by photogenerated holes of the hydrogen-evolving photocatalyst. In the last decade, solid redox mediators like reduced graphene oxide,^[69,70] carbon,^[71] and metals^[72] became more prominent for Z-scheme water splitting.

The most prominent example for such a Z-scheme is the photocatalyst sheet by Domen and co-workers,^[23] which is based on using gold metal below immobilised molybdenum-doped BiVO₄ (BiVO₄:Mo) and SrTiO₃:Rh/La, and that can split water with an energy efficiency of 1.1 %, the maximum efficiency reported for this reaction with oxide powders so far. When carbon was used as base layer, an STH of 1.0 % could be achieved.^[71] The system was recently further optimised by using a gold colloid and a zirconium oxide coating.^[73]

Oxynitrides are another class of already mentioned visible light absorbing materials for water splitting, however many of them are not able to split water alone. In combination in Z-schemes, many have been reported active for water splitting.^[74–76] For example, MgTa₂O_{6-x}N_y/TaON or BaMg_{1/3}Ta_{2/3}O_{3-x}N_y/Ta₃N₅ heterostructures were combined with PtO_x-WO₃ for Z-

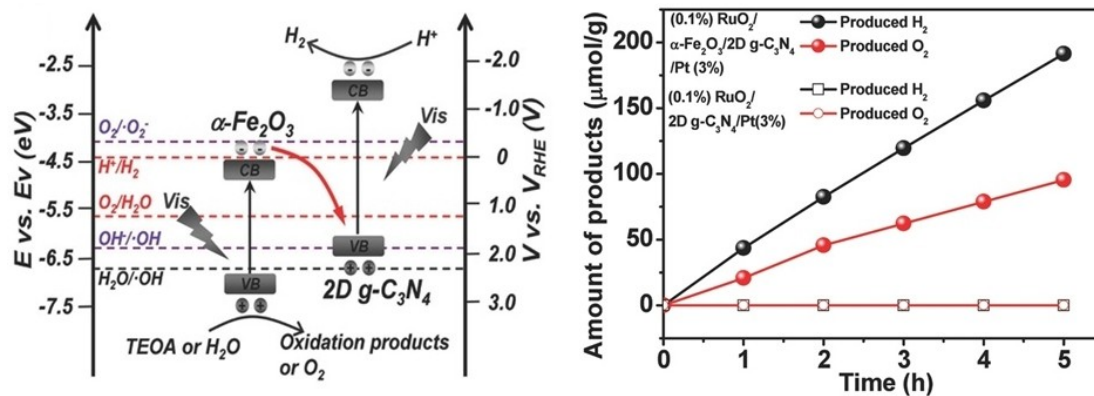


Figure 3. left: Energy band diagram of Z-scheme mechanism in $\alpha\text{-Fe}_2\text{O}_3/2\text{D g-C}_3\text{N}_4$ hybrids at pH=0; right: Time course of H_2 and O_2 evolution using (0.1%) $\text{RuO}_2/\alpha\text{-Fe}_2\text{O}_3/2\text{D g-C}_3\text{N}_4/\text{Pt}$ (3%) under visible light irradiation ($\lambda > 400$ nm). Reaction conditions: photocatalyst 0.05 g; light source: 300 W xenon lamp fitted with a cutoff filter. Reproduced from ref.[90]

scheme water splitting.^[77,78] Combinations of oxynitrides with BiVO_4 turn out to be very effective for water splitting, as shown in 2018 for $\text{Rh}_y\text{Cr}_{2-y}\text{O}_3\text{-ZrO}_2/\text{TaON}$ combined with $\text{Au}/\text{CoO}_x\text{-BiVO}_4$.^[79]

Oxysulfides^[80] and oxychlorides^[81] were also utilized in Z-scheme water splitting, and BiVO_4 could also be combined with sulfides or oxysulfides for Z-scheme water splitting.^[70,82,83] Combinations of BiVO_4 with other visible light absorbing oxides include materials like CaFe_2O_4 ^[84] and ZnRh_2O_4 ^[85] for visible light overall water splitting.

In recent years, $\text{g-C}_3\text{N}_4$ has been frequently utilized for Z-scheme water splitting. Combinations with WO_3 ,^[86] TiO_2 ,^[87] and Fe_2O_3 ^[88] have been reported recently.

Recently, the combination of 2 two-dimensional absorber material became a new trend to enhance the interfacial contact Z-scheme photocatalysts for charge transfer.^[89] For overall water splitting, only very few examples of this mesostructured Z-schemes have been reported, namely black phosphorus (BP)/bismuth vanadate (BiVO_4),^[89] $\alpha\text{-Fe}_2\text{O}_3$ nanosheets with exfoliated of $\text{g-C}_3\text{N}_4$ (Figure 3),^[90] and BiVO_4 combined with $\text{g-C}_3\text{N}_4$.^[91]

4. Conclusion and Outlook

From an outside perspective, it might seem that materials for photocatalytic overall water splitting have become more and more complex to get to the "holy grail", hydrogen and oxygen evolution from water. Starting with one binary oxide getting to others, further to ternary and quaternary oxides, doping, oxynitrides and oxysulfides, and finally combination of those to Z-schemes, this impression seems viable. On the contrary, the increase in complexity goes in line with more and more complex compositions in our everyday technologies, but more importantly this felt increase in complexity came with a knowledge-based improvement on inorganic materials properties. The development for photocatalytic water splitting with mixed-anion materials and high-QE materials is very promising for this field, especially now after 50 years of materials research.

Of course, there are still some challenges to overcome. The solar-to-hydrogen efficiency of photocatalytic water splitting is still far too low to compete with other technologies for hydrogen generation, which also depends on the absorber material used. A theoretical 10% solar-to-hydrogen efficiency can only be achieved with single absorbers of a band gap smaller than ~ 530 nm, better 600 nm.^[92] Moreover, most of the reported water splitting materials only work with the modification of rare and noble element co-catalysts. In the light of sustainable and green chemistry, the amounts of critical elements have to be reduced further, and alternatives have to be found, not only in the co-catalysts for water splitting. In the same light, many of the reported materials need high temperature or long reaction times for their preparation. Green syntheses of new materials for water splitting have to be investigated, so that the evolved hydrogen can be considered a sustainable energy carrier.

Photocatalytic water splitting can be a cheap and environmental friendly way to generate this green energy carrier, and this Minireview has summarized some major materials design strategies of the last decades, which need to be considered moving forward, for the future knowledge-based improvement of inorganic photocatalyst materials for overall water splitting.

Acknowledgements

The author would like to thank Prof. Bernd M. Smarsly (Justus-Liebig-University Giessen) for many valuable discussions and his constant support in the last years. The German Research Foundation DFG is gratefully acknowledged for funding in the Emmy-Noether program (MA 5392/3-1). Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Photocatalysis · Semiconductor materials · Water splitting

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Manuscript received: April 1, 2021
Revised manuscript received: May 14, 2021
Accepted manuscript online: May 18, 2021