Chapter

On the Limits of Photocatalytic Water Splitting

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Abstract

The major drawbacks on the limited H₂ and O₂ evolution activities of one-step photocatalytic water splitting systems are given here with the emphasis on charge recombination, back-oxidation reactions, and mass transfer limitations. Suppression of these unwanted phenomena is shown to be possible with the usage of small crystal-sized photocatalysts with low defect concentrations, presence of phase junctions, selection of co-catalyst that would be active for H₂ evolution but inactive for O₂ reduction, coating of the co-catalyst or the whole photocatalyst with selectively permeable nanolayers, and usage of photocatalytic systems with high solid–liquid and liquid–gas surface areas. The mass transfer limitations are shown to be important especially in the liquid–gas interfaces for agitated and suspended systems with estimated H₂ transfer rates in the range of ~200–8000 μmol/h.

Keywords: hydrogen production, photocatalyst, water splitting, mass transfer, back-oxidation

1. Introduction

Hydrogen gas is one of the best alternatives to fossil fuels since it has a high gravimetric energy density (142 MJ/kg) and it produces zero carbon upon combustion. Hydrogen is also used as a major reactant in environmentally important reactions such as carbon dioxide hydrogenation to methanol [1] or ammonia production (Haber-Bosch reaction) [2]. For hydrogen to be used as a clean energy source, its production via renewable ways is of great importance. It is conventionally produced via steam reforming of methane and fossil fuels (energy intensive, \( \Delta H^0_{\text{rxn}} = 206 \text{ kJ/mol}, 700–1100^\circ\text{C} \) [3]) and coal gasification, which results in significant amounts of carbon dioxide production. The renewable ways for carbon-free production include biological sources (microalgae and cyanobacteria) and electrolysis of water using wind energy and photovoltaic cells as electricity generation sources. In addition to the mentioned renewable ways, photocatalytic water splitting/oxidation is a promising alternative, in which solar energy is used as the driving force to split water molecules to hydrogen and oxygen on the surface of a catalyst. This renewable production method of hydrogen is advantageous over other renewable methods due to the free source of energy and lower cost of the photocatalysts when compared to that of photovoltaic cells or wind turbines. Solar-driven catalytic (photocatalytic) reactions are considered to be of fundamental importance to the catalysis community since the solar energy is inexhaustible; i.e., the solar energy absorbed by the lands and oceans on an hourly basis (432 EJ/h)
or 120,000 TW [4]) is comparable to the Earth’s yearly energy consumption (reaching 575 EJ/year or 18 TW in 2017). However, the solar-to-hydrogen energy conversion value for photocatalytic water splitting systems is much lower (targeted to be 10%, currently reaching 1% [5]) than that of photovoltaic-assisted electrolysis (reaching 30% [6]) due to the major drawbacks in the one-step photocatalytic water splitting systems. Herein, we firstly introduce photocatalytic water splitting systems and give the major developments in materials such as visible light utilization and corresponding H₂ and O₂ production activity values (in Section 2). Then in Section 3, we discuss the causes of the low efficiencies in photocatalytic water splitting systems and the recent approaches in preventing energy efficiency-lowering factors such as inefficient visible light utilization, charge recombination, back-oxidation reactions, and mass transfer limitations.

2. Photocatalysis and water splitting

The first report on water splitting via harvesting photon energy is authored by Fujishima and Honda using a photoelectrochemical cell with a TiO₂ photoelectrode [7]. Following this first report suggesting the oxidation of water molecule via photogenerated holes on TiO₂ surface with the aid of small electrical voltage, photocatalytic water splitting on powder photocatalyst particles is demonstrated by other authors in the late twentieth century [8–15]. Metal-loaded semiconductors (such as Pt/TiO₂) are described as “short-circuited photoelectrochemical cells” that provide both the oxidizing centers and the reduction centers on the same catalyst (see Figure 1) [16].

Photocatalytic reactions are initiated by absorption of light having an energy higher than (or equal to) the bandgap of the photocatalysts that consist of semiconductor materials. This bandgap energy should be larger than 1.23 V for overall water oxidation reaction, for which the maximum of the valence band and the minimum of the conduction band should be located at proper potentials for the oxygen and hydrogen evolution reactions to occur. To illustrate, the minimum of

![Figure 1](image.jpg)

Schematic representation of photocatalytic water splitting on metal-loaded semiconductor particle systems: (1) light absorption and charge excitation from valence band to conduction band, (2) transfer of the photogenerated electrons and holes to the catalyst surface, (3) surface redox reactions, and (4) charge recombination.
the conduction band energy level should be located at a more negative potential than 0 V vs. NHE, at pH = 0 for H₂ evolution (Eq. (1)), and the maximum of the valence band should be at a more positive potential than 1.23 V vs. NHE at pH = 0 for oxygen evolution reaction (Eq. (2)):

\[
\begin{align*}
4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2 \quad (1) \\
2\text{H}_2\text{O} + 4\text{H}^+ + 4\text{e}^- & \rightarrow 4\text{H}_2 + \text{O}_2 \quad (2)
\end{align*}
\]

Following the light absorption, photoexcited electrons are transferred to the conduction band, while a positively charged charge carrier (hole) is generated at the valence band. These charge carriers are then transferred to the catalyst surface (step 2 in Figure 1) to be utilized in surface redox reactions, unless they recombine in the bulk or on the surface (step 4). Ultimately, electrons and holes reduce/oxidize the adsorbed species on the catalyst surface (step 3), the products of which should then be desorbed from the surface to complete the overall process.

2.1 Semiconductors

TiO₂, having a large bandgap (anatase: 3.2 eV), is the most commonly used photocatalyst due to its photostability, nontoxicity, and high activity (upon UV radiation $\lambda < 387$ nm). Following the report on water oxidation reaction [7], various photochemical reaction activities of TiO₂ such as carbon dioxide reduction with $\text{H}_2\text{O}$ [17–19], alkene and alkyne hydrogenation [20, 21], $\text{CH}_3\text{Cl}$ oxidation [22], 1-octanol degradation [23], phenol degradation [24], surfactant degradation [25], and more have been reported. Detailed reviews on TiO₂-based materials and photocatalytic performances can be found in literature [26–28].

As photostable and active TiO₂ is, UV light requirement to activate the large bandgap of TiO₂ motivated research for visible light active semiconductors as well as bandgap engineering for TiO₂ such as nonmetal ion doping (N [29], C [30], F [31], S [32]). Substitution of lattice oxygen atoms by these anions is reported to shift the valence band level upward and narrow the bandgap to as low as 2.25 eV ($\sim 550$ nm) with 16.5% N doping [33].

Similar to TiO₂, oxides of other transition metals with d⁰ (such as Ti⁴⁺, Zr⁴⁺, Nb⁵⁺, Ta⁵⁺, and W⁶⁺ [34, 35]) and d¹⁰ electronic configurations (such as Ga³⁺, In³⁺, Ge⁴⁺, Sn⁴⁺, and Sb⁵ [36–38]) are shown to possess large bandgap energies (>3 eV) due to the maximum valence band levels consisting O₂p orbitals located near 3 V (vs. NHE at pH = 0). These d⁰ and d¹⁰ metal oxide catalysts are reported to show remarkable one-step photocatalytic water splitting activity under UV light irradiation [39] reaching 71% quantum yield with photocatalysts such as Al-doped SrTiO₃ [40] or Zn-doped Ga₂O₃ [41]. The H₂ and O₂ evolution activity under UV radiation and the apparent quantum yields of some of these materials are given in Table 1. The apparent quantum yield is defined as the number of reacted electrons and holes divided by the number of incident photons on the photocatalysts. Table 1 is not intended to cover the whole range of particulate catalysts in literature but rather to give a selection of examples. A wider selection of d⁰ and d¹⁰ metal oxide particulate catalysts’ one-step water oxidation activity and apparent quantum yields can be found in the works of Kudo et al., Chen et al., and Domen et al. [39, 42, 43].

The most remarkable upgrades in the apparent quantum yields are achieved by material engineering such as (i) doping the metal oxides/perovskites with cations having lower valences, (ii) decreasing the crystal sizes to submicron levels, and (iii) loading with H₂/O₂ evolution co-catalysts.
Co-catalysts

An important addition to the light-harvesting semiconductors is H₂ evolution/O₂ evolution co-catalysts on the surface. The early co-catalysts that have been widely used included the noble metals and transition metal oxides such as Pt [12, 13], Rh [10], Ru [48], Au [49, 50], and NiOₓ [11] that mainly promote the hydrogen evolution, and CoOₓ [51] and Fe [52], Mn [52], RuO₂ [53], and IrO₂ [54] that accelerate the oxygen evolution. These metals are considered to act as charge carrier sinks that suppress electron–hole pair recombination as well as increasing the reaction kinetics by lowering the activation energy of the redox reactions. Co-catalysts are also known to inhibit photodegradation of the photocatalysts such as oxysulfides and oxynitrides by generated holes due to the effective extraction of these holes by the co-catalysts [55, 56].

Following the works of noble metal co-catalysts, Domen et al. showed water splitting activity on SrTiO₃ photocatalyst together with the co-catalyst NiO [57, 58], which became the choice of H₂ evolution co-catalyst for many d⁰ and d¹⁰ metal oxides such as La₂Ti₂O₇:Ba [44], La₄CaTi₅O₁₇ [59], Rb₂Nb₆O₁₇ [60], NaTaO₃ [46], and Ga₂O₃:Zn [47]. The photocatalyst stability of NiO-loaded K₂La₂Ti₃O₁₀ is reported to increase by addition of a second co-catalyst, Cr, using a co-impregnation method [61]. Based on the promoting effect of Cr, a systematic study of Cr and various transition metals (such as Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt) on (Ga₁₋ₓZnₓ)(N₁₋ₓOₓ) has been conducted [62], from which core-shell structures of core Rh nanoislands and shell Cr₂O₃ structures (10–30 nm in size) are found to promote H₂ and O₂ evolution reactions to significant levels [63].

Visible light utilization

The alterations to the semiconductors such as doping with low-valence cations, reducing particle sizes to submicron levels and obtaining a high degree of crystallinity help with the overall water splitting activity. However, activation of these photocatalysts uses a narrow portion of the solar spectrum (4%); i.e., the UV light sustains as a problem due to the large bandgap energies of these materials. To enable visible light utilization of the d⁰- and d¹⁰-type oxide semiconductors and to split water into H₂ and O₂ via one-step excitation, the valence band levels should be

| Semiconductor | Co-catalyst | Bandgap (eV) | H₂ activity (µmol/h) | O₂ activity (µmol/h) | AQY (%) | Reference |
|---------------|------------|--------------|----------------------|----------------------|---------|-----------|
| La₂Ti₂O₇:Ba   | NiOₓ       | 3.26         | 5000                 | 50                   | 30 at 300 nm | [44]    |
| SrTiO₃:Al     | Rh₂₋ₓCrₓO₃ | 3.2          | 550°                 | 280°                 | 56 at 365 nm | [45]    |
| SrTiO₃:Al     | Rh₂₋ₓCrₓO₃ | 3.2          | 1372°                | 683°                 | 56 at 365 nm | [45]    |
| SrTiO₃:Al     | MoO₂/RhCrO₃| 3.2          | 1800°                | 900°                 | 69 at 365 nm | [40]    |
| SrTiO₃:Al     | NiO        | 4.0          | 3390                 | 1580                 | 20 at 270 nm | [46]    |
| SrTiO₃:La     | NiO        | 4.1          | 19,800               | 9700                 | 56 at 270 nm | [34]    |
| Ga₂O₃:Zn     | NiO        | 4.4          | 4100                 | 2200                 | 20       | [47]    |
| Ga₂O₃:Zn     | Rh₀₋ₓCrₓO₃ | 4.4          | 32,000               | 16,000               | 71 at 254 nm | [41]    |

*0.1 g of photocatalyst is used instead of 1 g.

Table 1. H₂ and O₂ evolution activity of d⁰ and d¹⁰ metal oxide particulate catalysts under UV light irradiation.
shifted upward without changing the conduction band potentials. One approach to do this is to use oxynitrides to make use of N$_{2p}$ states that lie at a more negative potential than O$_{2p}$ states. Emerging LaMgTa$_{1-x}$O$_{1+3x}$N$_{2x}$ [64] and Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ [65] oxynitrides are representatives of visible light active overall water splitting catalysts. Using N doping, the absorbed light wavelength can be increased up to 500 nm on solid solutions of GaN:ZnO (Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$) [66] and up to 600 nm on solid solutions of LaTaON$_2$ and LaMg$_{2/3}$Ta$_{1/3}$O$_3$ (LaMgTa$_{1-x}$O$_{1+3x}$N$_{2-3x}$) [64]. Other examples include LaSc$_x$Ta$_{1-x}$O$_{1+2x}$N$_{2-2x}$ [67] and CaTaO$_2$N [68] in which La or Ta sites are replaced by Ca and Sc that alters O/N ratios due to charge compensation, which in turn results in valence band energy level shift.

Some examples of visible light active photocatalyst and their H$_2$ and O$_2$ evolution activity are given in Table 2. As it can be seen from the table, one-step water splitting quantum yields are quite lower when compared to those of the UV-activated photocatalysts (Table 1). The exceptions to the low activity are reported by Rh$_{2-y}$Cr$_y$O$_3$ (Rh 1.0 wt%, Cr 1.5 wt%)-loaded (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) photocatalyst [63], multiband InGaN/GaN nanowire arrays [69], and monodisperse 4 nm graphite nanoparticle-deposited C$_3$N$_4$ catalysts [70].

An alternative way to cover both oxidation and reduction reactions with semiconductors that could be activated under visible light radiation is to utilize two individual photocatalysts with an electron transfer mediator to obtain two-step excitation known as the two-step water oxidation (“Z-scheme system,” see Figure 2). In this system, O$_2$ evolution photocatalysts oxidize the water molecules to O$_2$, while the photo-generated electron is transferred to the mediator to reduce the electron acceptor (such as Fe$^{3+}$ ions or IO$_3^-$ ions). Then, the reduced mediator is oxidized by donating its electron to the H$_2$ evolution photocatalyst. At the same time, the photo-generated electrons in the H$_2$ evolution photocatalyst reduce H$^+$ to H$_2$.

The semiconductors used in this two-step water splitting process should be selected based on the energy levels of their corresponding valence or conduction band maximum/minimum that would enable O$_2$/H$_2$O oxidation and H$^+$/H$_2$ reduction. As H$_2$ evolution and O$_2$ evolution reactions are realized at separate photocatalysts, these semiconductors could have bandgap energy values lower than 3 eV that would enable visible light utilization such as Pt- or RuO$_2$-loaded WO$_3$.

| Semiconductor | Co-catalyst | Bandgap (eV) | H$_2$ activity (μmol/h) | O$_2$ activity (μmol/h) | AQY (%) | Reference |
|---------------|------------|-------------|------------------------|------------------------|---------|-----------|
| SrTiO$_3$:Rh,Sb | IrO$_2$ | 4.4 | 1.9 | 0.1 at 420 nm | [71] |
| g-C$_3$N$_4$ | Pt/CoO$_x$ | 2.8 | ~8.5 | ~3.5 | 0.3 at 405 nm | [72] |
| CDots-C$_3$N$_4$ | | 2.74 | 46 | 16 at 420 nm | [70] |
| Bi$_{1-x}$In$_x$V$_{1-x}$MoxO$_4$ | RuO$_2$ | 2.5 | 17 | 3.2 at 420 nm | [73] |
| BiYWO$_6$ | RuO$_2$ | 2.7 | 4.1 | 1.8 | 0.17 at 420 nm | [74] |
| LaMg$_{2/3}$Ta$_{1/3}$O$_3$N | RhCrO$_x$ | 2.7 | 927 | 460 | 5.9 at 420 nm | [76] |
| (Zn$_{0.18}$Ga$_{0.82}$) (N$_{0.82}$O$_{0.18}$) | Rh$_2$Cr$_y$O$_3$ | 2.64 | 38 | 21 | 12.3 at 400 nm | [69] |

Table 2. H$_2$ and O$_2$ evolution activity of one-step water splitting catalysts under visible light irradiation.
(E_g ~ 2.8 eV) or oxynitrides such as TaON (E_g ~ 2.4 eV) or Rh-doped SrTiO_3 (E_g ~ 2.4 eV). Examples of these materials and systems can be seen in Table 3. The detailed reviews on two-step photocatalytic water splitting can be found elsewhere [83].

### 3. Drawbacks on photocatalytic activity

There are numerous and challenging processes that need to be realized for photocatalytic evolution of H_2 and O_2 (Table 4) via a thermodynamically unfavorable reaction (Eq. (3)):

\[
H_2O \rightarrow H_2 + 1/2 O_2 \quad \Delta G^0 = 237 \text{ kJ/mol} \tag{3}
\]

These processes include (i) excitation of the semiconductor photocatalyst with photon having higher energies than the bandgap energy of the material, (ii) transfer of the photo-generated electrons and holes to the reaction sites on the surface, (iii) utilization of these charge carriers in the oxidation/reduction reactions, and (iv) desorption of the products from the surface of the photocatalyst to the liquid/gas medium.

As the timescale of these processes varies, recombination of the electrons and holes in the bulk or on the surface happens more frequently than the rate of the...
chemical oxidation/reduction reactions. Recombination is therefore considered to be one of the main reasons limiting the photocatalytic activity. Together with the recombination events, realization of back-oxidation reactions (Eq. (4)) on noble metals and the rate-limiting mass transfer events are the major drawbacks in an efficient photocatalytic process:

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \Delta G^0 = -237 \text{ kJ/mol} \quad (4) \]

Natural photosynthesis yields a much higher rate of O₂ evolution (see Table 4) when compared to artificial water splitting due to improved charge carrier and mass transfer events. From this comparison, it is clear that the photocatalytic systems still need to be perfected to compete with the nature’s intricate design.

### 3.1 Charge recombination

Due to the presence of the multiple processes, the overall photocatalytic reactions are extremely complicated. In order to obtain an efficient photocatalytic performance, the photo-generated charges must be transferred to the surface reaction sites as rapidly as possible while preventing recombination or trapping of these charge carriers. It is reported by Leytner and Hupp that 60% of the trapped electron–hole pairs recombine with a timescale of about 25 ns while releasing heat of 154 kJ/mol [85]. As the defects such as vacancies and dislocations are considered as recombination sites, higher crystallinity of the photocatalysts is often aimed to decrease the recombination rates. From diffusion point of view, the shorter distances for the charge carriers to the surface reaction centers are also aimed to prevent the recombination. Shorter pathways are achieved via smaller crystal/particle sizes of the photocatalysts. More than two times of increase in the H₂ and O₂ evolution rates on Al-doped SrTiO₃ photocatalyst (reaching an apparent quantum yield of 56% [45]) as the particle size drops from few micrometers to 200 nm is a direct evidence of the effect of the particle size. Another method for reducing the charge recombination is to make use of phase junctions. One example is the α-β-phase junction of Ga₂O₃, which results in enhanced interfacial charge transfer, charge separation, and therefore enhanced water splitting activity [86]. Loading the photocatalysts with co-catalysts such as noble metals or transition metal oxides to accelerate the reduction/oxidation reactions is a commonly employed method.

### Table 4

The processes occurring in photocatalytic water splitting on TiO₂ and their timescales [27] and the references therein.

| Process | Timescale |
|---------|-----------|
| Light absorption and electron and hole generation | Semiconductor $\rightarrow e^- + h^+$ | fs |
| Photo-generated electron and hole transfer to the surface and trapping | $h_{VB} \rightarrow h_{trap}$ | 200 fs |
| | $e_{CB} \rightarrow e_{trap}$ | 50 ps |
| Recombination of charge carriers | $e^- + h^+ \rightarrow \text{recombination}$ | $>20$ ns |
| Interfacial charge transfer | $e_{CB} + \text{O}_2 \rightarrow \text{O}_2^-$ | 10–100 μs |
| Observed O₂ evolution$^*$ | $2\text{H}_2\text{O} + 4h^+ \rightarrow \text{O}_2 + 4\text{H}^+$ | 37 s$^*$ |

$^*$Based on 16,000 μmol O₂/g/h O₂ evolution rate on Rh₀.₅Cr₁.₅O₃-doped Ga₂O₃:Zn upon illumination at 254 nm [41], assuming 10 m²/g surface area and 10¹⁵ sites/cm² site density.
These co-catalysts are known to enhance the charge migration from the semiconductor depending on the alignment of the potentials of the semiconductor and the co-catalyst. As these co-catalysts accelerate the desired H2 evolution and O2 evolution reactions, they can also increase the rates of undesired secondary reactions such as hydrogen oxidation or oxygen reduction to water reactions.

3.2 Back-oxidation reactions

Introduction of one-step photocatalysts for overall water splitting combined the H2 evolution and O2 evolution sites on the same catalyst surface. This design of a photocatalytic system that realizes both charge trapping and reduction/oxidation reactions on the same surface not only accelerated the charge recombination but also allowed secondary reactions on these reduction/oxidation centers. When fast removal of the products, i.e., H2 and O2, is not provided and there are no barriers that prevent interaction of these products with highly active sites, the reaction of H2 and O2 on the photocatalyst surface to produce H2O (2H2 + O2 → H2O) is highly probable. And back-oxidation of the produced H2 is considered to be one of the main reasons for observed low photocatalytic water splitting activity values.

As early as 1985, Sato and coworkers realized the importance of back-oxidation of H2 with O2 to produce H2O. They have realized that the metal-loaded photocatalysts, mainly Pt- or Pd-loaded TiO2, can oxidize H2 with O2 easily under the same photophysical water oxidation conditions. They have reported first-order reaction rate constants in the range of 0.23–0.51 h⁻¹ for Pt, 0.32–1.8 h⁻¹ for Pd, and 0.2–0.3 h⁻¹ for Rh, suggesting the least active metal for back-oxidation reaction to be Rh [10]. Later in 2000, Anpo and coworkers investigated back-oxidation reaction on Pt/TiO2 systems under dark conditions and observed increased back-oxidation rate with increasing Pt loading (up to 0.1 wt.% [87]). While Pt is active for H2 evolution (Eq. (1)), it is also notoriously active for dark H2–O2 recombination reaction (Eq. (4)) even at room temperature [88]. In order to prevent H2–O2 recombination reaction, the Pt surface is modified with F ions for Pt/TiO2 catalyst, and the reaction rate decreased from 2 to 0.3 h⁻¹ upon F⁻ modification [89]. The inhibition mechanism is suggested to be due to the occupation of the H2 surface adsorption sites on Pt by F atoms.

Another modification to the noble metal surfaces is reported by Lercher et al., in which CO is chemisorbed on the Rh co-catalyst for GaN:ZnO semiconductor. Chemisorbed molecular layer of CO suppressed the back-oxidation reaction by selective metal poisoning of the back-oxidation sites by CO. While H2 evolution rates of 28 μmol/h are achieved (75 mg photocatalyst, 300 W Xe lamp [90]), significant CO oxidation to CO2 is also observed.

The back-oxidation reaction-inhibiting effects of the nanolayer coating on noble metals are shown on Rh/Cr2O3-loaded GaN:ZnO photocatalysts. Rh/Cr2O3 core-shell structure [91] is formed by photodeposition of Rh and reduction of CrO4²⁻ by electrons coming from Rh upon radiation, resulting in few nanometer thickness of Cr2O3 layer (2–3 nm, see Figure 3). Hydrated Cr2O3 nanolayer is reported to selectively permeate protons for H2 evolution reaction [92], whereas it hinders O2 permeation from the layer inhibiting O2 reduction reaction (Eq. (5)) on Rh sites [93]. The same effect is also valid for Cr2O3-coated Pt catalyst (GaN:ZnO). Back-oxidation rates on Pt-loaded GaN:ZnO photocatalyst decreased significantly from ~105 × 10⁻¹² molecules/s to ~8 × 10⁻¹² molecules/s, while photocatalytic H2 evolution rate increased from ~5 × 10⁻¹² molecules/s to ~30 × 10⁻¹² molecules/s upon Cr2O3 coating [93]. Apart from the oxygen-blocking role of the Cr2O3 nanolayer, much lower back-oxidation rate of Rh-loaded GaN:ZnO when compared to Pt-loaded GaN:ZnO (11 × 10⁻¹² molecules/s vs. 105 × 10⁻¹² molecules/s)
explains the significant photocatalytic H₂ evolution activity on Rh/Cr₂O₃-loaded GaN:ZnO (130 × 10⁻¹² molecules/s). Lower back-oxidation rate of Rh-loaded GaN:ZnO could be related to the low-oxygen reduction reaction (Eq. 5) activity of Rh when compared to Pt [94]:

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O
\]

Similar selective permeability concept is considered to be the case for Ni/NiO core-shell structures deposited on various photocatalysts such as SrTiO₃ or NaTaO₃ [34, 57]. In these systems, in addition to the back-oxidation reaction impeding effect of NiO layer on Ni [58], low-oxygen reduction activity of NiOₓ catalysts when compared to Pt can also be considered to be effective for improved water splitting activity.

Coatings of the whole photocatalyst instead of the co-catalyst by oxyhydroxides of Ti, Nb, and Ta are reported on Rh-loaded SrTiO₃:Sc photocatalyst. Surface nanolayer not only suppressed back-oxidation reactions but also prevented the access of sacrificial agents such as ethanol to the photocatalyst surface, resulting in nearly stoichiometric H₂/O₂ ratios [95]. Surface nanolayer coatings on the whole photocatalysts have proven to also prevent photodecomposition (N₂ evolution) of oxyinitride photocatalysts while increasing the overall water splitting activity [64, 68].

Prevention of the secondary reactions such as H₂ oxidation or O₂ reduction reaction to H₂O is found to be essential for improving the overall water splitting activity and the apparent quantum yield values (reaching apparent quantum yield value of 69% under irradiation at 365 nm [40]). In addition to the reduced back-oxidation rates, complementary measures such as decreasing the charge recombination rates and enhancing the product transfer rates away from the surface (increasing the mass transfer rates) are necessary for increased photocatalytic water splitting activity.

3.3 Mass transfer limitations

Mass transfer limitations especially in the slurry photocatalytic systems can be the most overlooked problem in the photocatalytic field. To complete the
photocatalytic reaction cycle, adsorption of the reactants, reduction/oxidation of the reactants, desorption of the products, and transfer of the products from the photocatalyst surface to the gas phase need to be realized. When the rates of the mass transfer of the products from the surface are slower than the reduction/oxidation rates, produced H₂ and O₂ would stay longer on the surface, resulting in promotion of back-oxidation reactions. Moreover, when the mass transfer rates are slower than the reaction kinetics, the apparent H₂ and O₂ evolution rates in the gas phase will be limited by the mass transfer rates.

Experimental evidence for mass transfer limitations in agitated systems is presented in a previous publication [96]. In a batch slurry reactor, where the catalyst particles are suspended via agitation, observed H₂ evolution rates for UV-irradiated Pt/TiO₂ photocatalyst showed improvement with increasing stirring rates up to 900 rpm (Figure 4a). This improvement is a direct indication of mass transfer limitations on the solid–liquid and gas–liquid interfaces as the turbulence in the liquid and therefore boundary layers are affected by increasing stirring rates. In another experiment, the effect of liquid volume is investigated by varying catalyst

![Figure 4](image-url)

Figure 4.
(a) Effect of stirring rate on photocatalytic hydrogen evolution with methanol as sacrificial agent, with 0.5 wt% Pt/TiO₂, 250 ml deionized water, 2 ml methanol, (■) 900 rpm and (●) 350 rpm. (b) Observed hydrogen evolution rates in the gas phase with changing liquid volume, CH₃OH/H₂O:1/125 (v/v) and C_{catalyst}: 1 g/L for each case. Adapted from [96].
weight and liquid volumes (keeping the catalyst concentration constant). H₂ evo-
lation rates on an hour basis (μmol H₂/h) are found the same regardless of the liquid
volume (or catalyst weight) above 62.5 ml (Figure 4b) as the H₂ evolution rate per
gram and hour basis decreased as liquid volume increased. Similar H₂ evolution
rates regardless of the catalyst weight indicate significant mass transfer limitations
in the liquid–gas interface.

Mass transfer limitations for different photocatalytic reaction systems are ana-
lyzed by different groups. For immobilized photocatalyst systems, the importance
of internal mass transfer resistance is emphasized [97]. In another investigation,
severe mass transfer limitations are observed in the product separator (liquid–gas
interface) for a fluidized bed/separator system, in which modification of the liquid–
gas surface area enhanced the H₂ evolution rates by 350% [98].

To prevent mass transfer limitations in the photocatalytic tests and to report actual
kinetic rates; stirring rates, liquid levels, and mass transfer areas should be designed
carefully. To design these parameters, approximate mass transfer rates should be
known. Here, we present a sample calculation for H₂ mass transfer rate in a slurry
reactor containing 0.5 g TiO₂ photocatalyst having a surface area of 40 m²/g inside an
agitated glass reactor having 200 ml liquid volume and a tank diameter of 7 cm.

Mass transfer resistances in a gas–liquid–solid multiphase photocatalytic systems
involve the internal mass transfer, mass transfer from the solid catalyst particles to
liquid (Eq. 6), transfer from the liquid bulk to the liquid interface (Eq. 7), and
transfer from the liquid–gas interface to the gas phase (Eq. 8). Photocatalysts such
as perovskites and TiO₂ are known to be nonporous (unless mesoporous versions
are prepared on purpose [99, 100]) and have surface area values between 5 and
50 m²/g. For nonporous photocatalysts, the internal mass transfer limitations can be
discarded (Eq. 9). Hence, the H₂ mass transfer rate equation will have a form
containing the mass transfer resistances from the solid–liquid and liquid–gas inter-
faces as seen in Eq. 8:

\[
\begin{align*}
    r_{H₂,S} &= k_s a_S (C_S - C_L) \\
    r_{H₂,L} &= k_L a_L (C_L - C_{Li}) \\
    r_{H₂,G} &= k_G a_G (C_{Gi} - C_G) \\
    r_{H₂} &= \frac{CH₂ - HCH₂}{(1/k_{aS} + 1/k_{aL} + 1/k_{aG})} \\
\end{align*}
\]

The mass transfer limitations coming from the solid–liquid and liquid–gas inter-
faces may play important role depending on the photocatalytic reactor type. The most often used photocatalytic reactor systems such as slurry reactors have solid–
liquid and liquid–gas phase interfaces that suspend its catalysts by agitation using an
impeller or a magnetic stirrer. The convection mass transfer coefficient for solid–liquid
interface of such a system could be estimated using Eq. 10 suggested by
Armenante and Kirwan for agitated tanks using Kolmogorov’s theory for Reynold’s
number calculation to consider the effect of solid particle size [101]:

\[
Sh = \frac{k_s d_p}{D_{H₂-H₂O}} = 2 + 0.52 \text{Re}^{0.52} \text{Sc}^{1/3}
\]

where \( k_s \) is the convection mass transfer coefficient from solid to liquid in (m/s),
\( d_p \) is the particle diameter in (m), \( D_{H₂-H₂O} \) is the diffusion coefficient of H₂ in liquid
water (m²/s), and Sc is the Schmidt number. A rough estimation for \( k_s \) for such
system can be found in Table 5.
The creation of air/inert bubbles in the continuous phase (water) due to agitation could be considered as the transfer mechanism of produced H₂ from the liquid phase to the gas phase. In such systems, comparing the mass transfer resistance from liquid to interface and interface to gas, it can be assumed that nearly all of the mass transfer resistance comes from the liquid side of the interface [102], leaving Eq. 9 as Eq. 11:

\[ r'_{H_2} = \frac{C_{H_2,L} - C_{H_2,Li}}{\left( \frac{1}{k_{As}} + \frac{1}{k_{L,atL}} \right)} \]  

The liquid side mass transfer coefficient for such a system could then be calculated using Calderbank and Moo-Young correlation for rising small bubbles of gas in continuous liquid phase (Eq. 12) [103]:

\[ Sh = \frac{k_L d_b}{D_{H_2-H_2O}} = 2 + 0.31Ra^{1/3} \text{ where } Ra = \frac{d_b^3 (\rho_L - \rho_G) g}{\mu_L D_{H_2-H_2O}} \]  

The first term on Eq. 12 is the molecular diffusion term, whereas the second term is for the rise of the bubbles due to gravitational forces independent of the agitation. With estimations on the bubble size and gas holdup of such a system (given in Table 6), the mass transfer coefficient and \( k_{L,atL} \) term are calculated to be 2.5 \( \times \) 10⁻⁴ m/s and 2.2 \( \times \) 10⁻⁶ m³/s, rendering liquid–gas mass transfer resistance way more important than solid–liquid resistance.

The overall mass transfer coefficient and the mass transfer rate from solid to the gas phase can be calculated with the estimated \( k_{As} \) and \( k_{L,atL} \) values. As the concentration of H₂ in the gas phase will be negligible (\( C_{G} \rightarrow 0 \)), the liquid phase interface can also be assumed to be equal to zero (\( C_{H_2,Li} \rightarrow 0 \)) with negligible gas phase resistance. Therefore, from Eq. 11, the rate of H₂ mass transfer can be calculated by assuming H₂ concentration at the catalyst surface and the gas holdup ratio in the liquid. The rate of H₂ mass transfer values for 200 ml of water and 0.5 g of catalyst

| Parameter                          | Unit     | Value                      |
|------------------------------------|----------|----------------------------|
| Particle size, \( d_p \)          | \( \mu m \) | 1                          |
| Density of water, \( \rho_L \)    | kg/m³    | 997 at 25°C                |
| Viscosity of water, \( \mu_L \)   | Pa s     | 890 \( \times \) 10⁻⁶ at 25°C |
| Kinematic viscosity, \( \nu \)    | m²/s     | 8.93 \( \times \) 10⁻⁷     |
| Schmidt number \( (Sc = \frac{\nu}{D_{H_2-H_2O}}) \) |          | 141                        |
| Energy density, \( \varepsilon = \frac{\text{Power}}{\text{mass of liquid}} \) | m²/s³   | 25 for 5 W stirrer, 200 g solution |
| Reynold's number \( (Re = \frac{\varepsilon^{1/3} d_b}{\mu_L}) \) |          | 0.033                      |
| Sherwood number, \( Sh = \frac{k_L d_b}{D_{H_2-H_2O}} = 2 + 0.52 Re^{0.51} Sc^{1/3} \) |          | 2.46                       |
| Diffusion coefficient of H₂ in water | m²/s     | 6.30*10⁻⁹ at 25 °C         |
| Convection mass transfer coefficient for solid, \( k_s \) | m/s     | 0.015                      |
| \( k_{As} \) | m³/s | 0.31 |

Table 5. Convection mass transfer coefficient calculation for solid–liquid transfer and parameters used in the calculation.
are calculated in the range of ~200–800 μmol/h (see Figure 5) for a surface H₂ adsorption capacity range of 50–400 μmol/g (H₂ chemisorption on 0.1% Pt/TiO₂ is reported to be ~400 μmol/g at room temperature [104]) and gas holdup ratio between 0.001 and 0.005.

The H₂ concentration on the solid surface and the gas–liquid contact area are not easy to estimate. However, for the limited gas–liquid area, the photocatalytic reaction rates above the calculated mass transfer rate will be suppressed due to the limiting mass transfer rates. Therefore, special care must be given for the UV-irradiated photocatalytic systems, in which observed H₂ and O₂ evolution rates are found to be close to the calculated mass transfer rates here (see Table 1).

These studies show that for each type of photocatalytic system that contains limited gas–liquid contact area or immobilized photocatalyst, mass transfer limitations should not be underestimated, and not only the materials but also the systems should be improved for better photocatalytic efficiencies.

| Parameter                     | Unit    | Value       |
|-------------------------------|---------|-------------|
| Bubble size, dₘ               | μm      | 700         |
| Density of water, ρₗ           | kg/m³   | 997 at 25°C |
| Density of air, ρ₉             | kg/m³   | 1.18 at 25°C|
| Viscosity of water, μₗ         | Pa s    | 890 × 10⁻⁶  |
| Raleigh number (Ra = dₘ³ρₗ⁰ρ₉⁰gμₗDH²H₂O) | 5.97 × 10⁵ |
| Sherwood number, Sh = kₗdₘ / μₗDH²H₂O | 28.1   |
| Diffusion coefficient of H₂ in water | m²/s | 6.3 × 10⁻⁹  |
| Convection mass transfer coefficient for liquid, kₗ | m/s | 2.5 × 10⁻⁶ |
| Liquid–gas bubble contact area, aₗ = 6πρ₀dₘ / 3ρₗVₗ | m² | 0.008 (gas holdup, φ, assumed to be 0.005) |
| kₗaₗ | m³/s | 2.2 × 10⁻⁶ |

Table 6.
Convection mass transfer coefficient calculation for liquid–gas transfer and parameters used in the calculation.

**Figure 5.**
Calculated H₂ mass transfer rate values (μmol H₂/h) for gas holdup values of 0.001 and 0.005 and H₂ adsorption capacity values in the range of 50–400 μmol/g. The liquid volume is taken as 200 ml and catalyst weight is taken as 0.5 g.
4. Future of photocatalytic H₂ evolution

The literature examples of photocatalytic water splitting activities show improvements in visible light utilization, charge separation, and prevention of back-oxidation reactions via fine tuning of photocatalyst materials that enabled more efficient water splitting systems. The efficiency of these systems working under sunlight is better defined with solar-to-hydrogen energy conversion efficiency (STH), i.e., hydrogen production rate times the Gibbs free energy for generating 1 mole of H₂ divided by the power of incident sunlight (Eq. 13):

\[
\text{STH} = \frac{(\text{mmol } H_2/s) \times 237 \times 10^3 \text{ J/mol}}{P\left(\frac{\text{mW}}{\text{cm}^2}\right) \times A(\text{cm}^2)} \times 100 \tag{13}
\]

The estimated STH required for the particulate photocatalytic systems to be economically compatible with current H₂ production technologies is 10% [104]. However, the highest STH values obtained with current developed photocatalysts are in the order of 1–2% (1.8% at 400–475 nm using Rh/Cr₂O₃-loaded GaN:Mg/InGaN:Mg photocatalyst [69] and 2% at 420 nm using CDots-C₃N₄ [70]). The STH conversion efficiency depends both on the catalytic activity and the extent of the utilization of sunlight that depends on the bandgap of the semiconductor. With current photocatalysts having absorption edges around 500 nm, even 100% apparent quantum yields would not guarantee 10% STH values [106]. For a photocatalyst to show 10% STH values, it should have absorption edges at least at 600 nm with apparent quantum yields around 60%. Under the light of these calculations, it can be said that the present photocatalysts having adsorption edge values around 450 nm and quantum yields around 10% are far from being utilized in commercial systems. In order to achieve targeted STH values, the photocatalysts with lower bandgap energies such as (oxy)nitrides and (oxy)sulfides should be improved for H₂ evolution activities while ensuring their thermal stability and photostability.

Large-scale photocatalytic water splitting reactors are implemented with current low STH values as of 2015. The first example of large-scale photocatalytic water splitting utilized Pt-loaded C₃N₄ photocatalyst with sacrificial electron donor triethanolamine in a flat-panel-type photocatalytic reactor system in 2015 [107]. The solar-to-hydrogen conversion efficiency is reported to be 0.12%, for which the photocatalytic activity is monitored for 30 days. In such systems, where a sacrificial reagent such as triethanolamine or methanol is irreversibly oxidized at a more negative potential than water (thermodynamically more favorable) at the oxidation centers, the photo-generated charges can be more efficiently separated, thus increasing H₂ evolution rates. However, in those systems, hydrogen production is not solely due to the water splitting; as the carbon- and hydrogen-containing “sacrificial agents” are being oxidized at the oxidation centers, they produce hydrogen as well as aldehydes, carboxylic acid, and carbon dioxide [108].

Another large-scale photoreactor is reported by Domen et al., who used Al-doped and RhCrO₂-loaded SrTiO₃ photocatalyst sheets in their 1 × 1 m water splitting panel [45]. The achieved STH value under simulated sunlight is 0.6% at 331 K and limited to a maximum value of 1.4% due to the large bandgap energy of the photocatalyst (3.2 eV). Improved STH values (reaching 1.1%) are shown to be possible on a two-step excitation system in 2016 using photocatalyst sheets having smaller bandgap energy values such as Mo-doped BiVO₄ (2.4 eV) and La- and Rh-doped SrTiO₃ [5].
5. Conclusion

The developments in the photocatalytic water splitting reactions are explained here with the emphasis on the one-step photocatalysis systems. The early photocatalyst improvements with bandgap engineering, co-catalyst usage, and size reductions are shown to contribute to the increased visible light-driven H₂ evolution activity values. The main drawbacks in the present systems are discussed to be the charge recombination, back-oxidation reactions of the products into water, and mass transfer limitations especially in the three-phase systems. Using defect-free small crystals of photocatalysts and making use of phase junctions or metal co-catalysts are suggested to decrease charge recombination rates. Back-oxidation of H₂ into water or oxygen reduction reaction to water is expected in many noble metal-containing particulate photocatalyst systems. The prevention of these unwanted secondary reactions is shown to be possible to some extent by modification of the noble metal surfaces. Some examples of these modifications are anion coating, partial adsorption of a poison, or nanolayer coating of the co-catalyst or the whole photocatalyst. Selective permeation property of the nanolayer coatings such as Cr₂O₃ is reported to suppress the back-oxidation rates, resulting in enhanced H₂ and O₂ evolution rates. Possible mass transfer limitations, limiting the observed rates in three-phase systems, are predicted especially in the liquid–gas interfaces. The literature examples attracted attention for the liquid–gas interfaces in suspended systems and internal mass transfer limitations for the immobilized photocatalyst systems. It is concluded that, in addition to the required developments in activities with suppression of charge recombination, back-oxidation, and mass transfer limitations, future of the photocatalytic systems would necessitate active and stable photocatalysts with narrower bandgap energies (to be activated at >600 nm) for achieving targeted 10% solar-to-hydrogen energy conversion efficiency value.

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