Photocatalytic Overall Water Splitting Using Modified SrTiO_3

Kai Han

PHOTOCATALYTIC OVERALL
WATER SPLITTING USING
MODIFIED SRTIO₃

Kai Han

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Chapter 1

General introduction

1.1 Renewable energy and hydrogen production

The growth in energy demand of the world has recently been met by enhanced production of fossil-based fuels, including coal, oil, or gas (methane).^{1,2} As shown in Figure 1.1, renewable resources constitute a relatively small fraction of the combined world energy consumption.³ As a consequence, greenhouse gas emissions and environmental pollution have increased to unsustainable levels. Renewable energy sources need be implemented urgently, especially since further global development and growth are expected⁴. In development of a society based on renewable energy, hydrogen is identified as one of the potential energy vectors, since hydrogen has a high energy density, and utilization produces water. In fact, during 2011-2016, the estimated annual growth rate of the global hydrogen production was 5.6% and the global hydrogen market is expected to continue increasing².

Figure 1.1. The developments in total world energy consumption split on sources from 1800 to 2017.³

Nowadays, hydrogen is produced by methane steam reforming, which produces large amounts of the greenhouse gas CO_2 . Another method is the electrolysis of water, but this process is significantly more costly.^{2,5,6} To produce hydrogen effectively on the basis of renewable energy sources, the costs need to be reduced. Solar-light utilization for photocatalytic overall water splitting

(POWS) is a promising alternative to electrolysis to produce hydrogen, since photocatalytic water splitting is simple, and can be operated at low-cost.^{1,4,7} Transformation and storage of solar energy in the form hydrogen can significantly reduce the rate of the greenhouse gas emissions. Given the low-cost and simplicity of photocatalytic hydrogen production, this thesis has focused on designing an efficient photocatalytic water splitting system. In fact, there are three main categories of Photocatalytic hydrogen production: photovoltaic-assisted electrolysis (PV-E), photocatalysis, and photoelectrocatalysis.⁸

1.2 Photocatalytic water splitting

1.2.1 Principles for photocatalytic water splitting

In POWS, a semiconductor (generally called photocatalyst) absorbs photons and generates charge carriers (electrons and holes), initiating the reduction and oxidation reactions on the surface. In the past decades, the field of POWS has experienced various developments and is now considered a multidisciplinary research field. Semiconductor physics, electrochemistry, theoretical simulation and many other scientific disciplines now engage in the research.^{7,9–11}

Overall water splitting is a thermodynamically uphill reaction with a standard Gibbs free energy (ΔG^0) of 237 kJ/mol.¹² Three steps are involved in this process (figure 1.2): i) the photocatalysts absorbs light to produce charge - carriers; ii) charges separate and move to the surface of the semiconductor; iii) redox reactions consume the charge carriers at the surface.¹³ For industrial applicability and feasibility, a POWS system must have a Solar-to-hydrogen (STH) efficiency greater than 10%., which is equivalent to a minimum photocurrent density of 8 mA/cm². The efficiency of each step contributes to the overall performance (Figure 1.2). Therefore, it is critical to consider all three steps when designing a photocatalysts. In this thesis, significant attention is paid to step iii), charge transfer and minimizing kinetic barriers of the desired redox reactions (reduction of water (protons) and oxidation of water (yielding oxygen)).

Figure 1.2. Schematic illustration of semiconductor-based POWS.

When exposing a semiconductor to some external environment (electrolyte, metal, et al.), charge-transfer at the interface causes band bending. Fig. 1.3 displays the energy levels of an n-type semiconductor, and illustrates the charge-transfer process. Typically, when the Fermi level of the semiconductor is higher than the redox potential of the electrolyte (or the electrolyte function (ϕ_m) is higher than that of the semiconductor (ϕ_s)), electrons will transfer from semiconductor to electrolyte till the Fermi level is equilibrated with the redox potential of the electrolyte.^{14,15} After reaching equilibrium, the semiconductor will be positively charged at the interface due to the formation of a Helmholtz layer by the trapped electrons, and absorbed ions. The generated low concentration of free charge carriers at the interface of the semiconductor forms a new build-in electronic field, due to the depletion of free charge carriers near the surface of the semiconductor, as compared to the bulk. This newly formed field is also called space charge layer or depletion layer^{7,15}, and is very useful for understanding how the electric structure of a semiconductor is changed when doped with other elements or modified with co-catalysts.^{8,12}

In terms of n-type semiconductors, the accumulation of electrons on the surface leads to upward band bending. This upward bending will drive the holes to the surface of the semiconductor, which can then induce oxidation reactions, whereas the downward bending of p-type semiconductors will be suitable for reduction reactions. In fact, a non-functionalized semiconductor typically shows

a low catalytic efficiency due to low surface redox reaction efficiency, increasing probability of charge carrier recombination^{7,16}. To improve the photocatalytic efficiency, effective approaches have been developed, such as producing new semiconductor materials and introducing co-catalysts on the surface.

Figure 1.3. Schematic illustration of the band bending in semiconductor.

1.2.2 Requirements for photocatalysts

Various photocatalysts have been developed and have shown potential in performing the water splitting reaction to produce hydrogen. In particular, some oxide materials having the d^0 or d^{10} electronic configurations allow for POWS (Figure 1.4).⁴ One of the crucial aspects determining the photocatalytic performance is the position of the valence band (VB) and conduction band (CB).¹⁷ The energy difference between the valence band (VB) and conduction band (CB) determines the light absorption properties, while the positions also define the feasibility of surface redox reactions. During a photocatalytic process, the electrons and holes are generated in the conduction band (CB) and valence band (VB), respectively. Then the surface redox reactions take place once the charge carriers (electrons and holes) have reached the surface of the photocatalyst. To efficiently complete POWS reactions, semiconductors must meet the following requirements:

- ❖ A band gap larger than 1.23 eV to be thermodynamically favorable for POWS. Specifically, the Schottky-Queisser limit suggests a the optimal band value of the semiconductor is between 2 and 2.4 eV.
- ❖ The band energy positions should be higher than the redox potential of the electrolyte: $E_{cb} > E_{red}$ and $E_{vb} > E_{ox}$.
- ❖ The mobility and lifetime of the charge carriers should be effieicnt to migrate to the surface of the photocatalyst.
- ❖ Have a high absorption cross section, and minimal charge carrier recombination.
- ❖ The photocatalyts must be stable under illumination.
- ❖ Ideally made from earth abundant and economically inexpensive materials.

Figure 1.4. Band gap structure of some semiconductors, used as photocatalysts.

1.2.3 $SrTiO_3$ as the photocatalyst material

Among the many developed photocatalysts, perovskite photocatalysts have shown their ability for POWS.¹⁸ Perovskite materials have a general formula ABO_3 , where A is an alkaline-earth-cation and B is a tetravalent transient metal cation (figure 1.5), such as $BaTiO_3$, $NaTaO_3$, and $SrTiO_3$.¹⁹ For these structures, introducing new heteroatoms on either an A or B site will lead to changes in 3d

electron interactions, eventually tuning the valence state and electronic structure of the perovskite material. For example, through tuning the $\text{La}^{3+}/\text{Sr}^{2+}$ ratio in $\text{La}_{1-x}\text{Sr}_x\text{BO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{BO}_4$ ($\text{B} = \text{Fe}, \text{Co}, \text{Mn}, \text{or Ni}$) oxides, Patzke and co-workers²⁰ showed a transition from insulating to metal-like behavior, allowing optimization for photocatalytic water oxidation reaction.

Figure 1.5. The ideal cubic perovskite structure of ABO_3 . (Reprinted with permission from Ref. 14)

SrTiO_3 is a cubic perovskite with an indirect band gap of 3.2 eV.²¹ Under UV illumination, SrTiO_3 , modified with a co-catalyst such as Pt, Rh or NiO_x , can split water with a stoichiometric ratio of H_2 and O_2 .^{22,23} Domen and co-workers deposited core-shell Ni@NiO_x co-catalyst on the surface of SrTiO_3 , explaining the catalytic function by enhancement of the hydrogen evolution reaction by Ni-particles.²¹ Doping of foreign elements (Rh, Ir, or Cr) into the structure of SrTiO_3 , induces a mid-gap state in the band structure, which allows visible light absorption.^{24–27} For instance, Rh doped SrTiO_3 showed a high photocatalytic water splitting efficiency induced by visible light.²⁸ Besides improvement in the optical properties, flux-treatment in SrCl_2 was used to improve crystallinity of SrTiO_3 , to change the particle morphology, and introduce dopants (mainly Al), thereby significantly increasing the apparent quantum yield at 360 nm to 30%.²⁹ At the same time, the same group of researchers reported a similar increase in AQY by simple impregnation of as-prepared SrTiO_3 with various different metal salts, inducing diffusion of the metal ion into the SrTiO_3 particles by high

temperature annealing.³⁰ Essentially, tuning the capability of SrTiO₃ in photocatalytic water splitting is feasible by altering the chemical composition and/or physical appearance.

In this thesis, SrTiO₃ is selected as the photocatalyst, and doped with Mg or Al, to modify the chemical and physical properties and study the effect of dopants on the performance in the POWS reaction.

1.2.4 Engineering with co-catalysts

A typical composite photocatalyst is comprised of a semiconductor substrate and a surface-deposited metal (oxide) co-catalyst. The identified role of the co-catalysts is to achieve photocatalytic water splitting reactions by promoting surface reactions (the efficiency of catalysis, η_{cat}), tackling the third step of POWS (surface redox reactions consuming the charge carriers) outlined in section 1.2.1. Noble metals (e.g. Pt, Rh, Ru, and Au)^{31–34}, metal sulfides (e.g. MoS₂, NiS)^{35,36}, and metal oxides (e.g. NiO, CuO)^{37–39} are well known water reduction catalysts. In contrast, some metal oxides (e.g. IrO_x, MnO_x, and CoO_x)^{40–43} and metal hydroxides (e.g. NiOOH, FeOOH)^{44,45} often serve as the water oxidation catalysts. In addition, some noble metals (e.g. Pt, Au, Pd)^{46–48} and metal oxides (e.g. CuO, Cu₂O)⁴⁹ have recently been reported to enable the CO₂ reduction reaction.

It is important to emphasize that co-catalytic nanoparticles are not thermally activated in photocatalysis, but rather by the charge carriers in the semiconductor produced by light absorption. The charge carriers migrate across the interface of the applied semiconductor and the metal(oxide) nanoparticles. After successful transferring of charges to such co-catalysts, redox reactions take place, which are facilitated by lowering of the over-potential of electron transfer reactions, similar to electrocatalysis.^{50–52}

In this thesis, Ni/NiO or RhCrO_x have been used as co-catalysts. Additionally, the role of Cr₂O₃ is studied when combined with the Ni/NiO co-catalyst. Photocatalytic water splitting has been performed in a CSTR (Continuously Stirred Tank Reactor), which will be demonstrated to be extremely useful to observe transients in catalyst composition.

1.3 Photocatalytic water splitting set-up

Figure 1.6. Schematic representation of the applied set-up to study water splitting. The exhaust of a continuously purged reactor is analyzed by a Micro-GC.

The photocatalytic water splitting measurements are conducted by dispersing a particular amount of photocatalyst powder into pure water. The produced gases (H_2 and O_2) are detected and analyzed by gas chromatography (figure 1.6). A continuously stirred tank reactor (CSTR) fed with a constant flow of helium carrier gas was used.²⁸ By doing this, it is possible to detect photocatalytic gas production with a minute time resolution, and the observed photocatalytic transients are useful to determine how the photocatalyst species change during illumination time.

The gas chromatograph used is a CompactGC (Interscience B.V.) equipped with a pulsed discharge detector (PDD). This type of detector is using a stable, low powered DC discharge in helium as an ionization source. Due to this helium ionization, the minimum detectable quantity can reach the ppb (10^{-9}) level. During the photocatalytic water splitting measurement, a constant, 10 mL/min helium gas flow is purged through the slurry solution containing the photocatalyst. For GC detection, a 50 μL sample is taken, and the concentration of the compound is automatically calculated based on the prepared calibration.

The light source for the photocatalytic measurements is an ABET Technologies model 10500 Low Cost 1.5 AM solar simulator, and photocatalytic measurements are performed in a 25 mL optical glass cuvette (402.013-OG, Hellma).

1.4 Aims and outline of this thesis

As outlined above, perovskite-based semiconductors and particularly SrTiO_3 are known to be materials that facilitate overall water splitting under UV light illumination. Modification of the surface with a suitable nanoparticulate co-catalyst, such as Pt or Ni/NiO core-shell structures, is still indispensable as co-catalysts decrease energy barriers. Thus, to a large extent the interface between a co-catalyst and a semiconductor as well as the stability during operation of the co-catalyst itself determine the activity of the overall composite photocatalyst (semiconductor/co-catalyst). So far limited knowledge about the co-catalyst stability are available and a detailed understanding must be achieved. In fact in earlier work it was noted that transients in hydrogen and oxygen evolution result from changes of the co-catalyst during operation.

In this case, the central scientific question addressed in the context of this thesis is: **How stable are co-catalysts, particularly Ni/NiO and Pt nanoparticles, in aqueous environmental under illumination and to what extent can the stability of a co-catalysts/semiconductor composite be influenced by means of surface, interface and bulk modifications of the material.**

In this thesis, the performance of SrTiO_3 is discussed in the POWS reaction, and various modifications have been applied to improve the photocatalytic water splitting efficiency, including loading with different co-catalysts (Pt, NiO_x and RhCrO_x) and doping with foreign elements (Mg, Al). The photocatalytic transients of the modified SrTiO_3 photocatalysts are collected in the continuously stirred tank reactor (CSTR). Through understanding of the photocatalytic transients, changes in composition of the photocatalyst species can be easily observed.

This thesis has been categorized in the following chapters:

In **Chapter 2**, the performance of core/shell structured Ni/NiO_x co-catalysts, deposited on the surface of SrTiO_3 , in the photocatalytic water splitting is shown. Transients in composition of Ni/NiO_x core-shell co-catalysts are discussed on the basis of state-of-the-art continuous analysis of photocatalytic water-splitting, and *post* XPS and TEM analyses. The formation of excessive

hydrogen ($\text{H}_2 : \text{O}_2 \gg 2$) in the initial stages of illumination demonstrates oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH (Nickel Oxy Hydroxide). A disproportionation reaction of Ni and NiOOH , yielding $\text{Ni}(\text{OH})_2$ with residual embedded Ni, occurs when illumination is discontinued, explaining repetitive transients in (excess) hydrogen and oxygen formation when illumination is re-initiated.

In **Chapter 3**, a simple solid state preparation method is applied to control the incorporation of magnesium into the perovskite structure of SrTiO_3 . After deposition of appropriate co-catalysts like Pt or Ni/NiO, the photocatalytic water splitting efficiency of the $\text{Mg}:\text{SrTiO}_x$ composite is up to 20 times higher compared to SrTiO_3 containing similar catalytic nanoparticles, and an apparent quantum yield (AQY) of 10 % can be obtained in the wavelength range of 300 - 400 nm.

In **Chapter 4**, an additional Cr_2O_3 film is photodeposited on top of Ni/NiO_x- $\text{Mg}:\text{SrTiO}_3$ to improve the stability and photocatalytic activity. Owing to the anti-corrosion function of Cr_2O_3 , leaching of Ni and Mg was considerably suppressed. Under optimal conditions, an apparent quantum efficiency of 30% was achieved under 365 nm LED light illumination, and the stability was maintained for over 70 hours. Detailed investigation demonstrates that Cr_2O_3 mainly serves to protect the elements against leaching instead of avoiding the oxidation of hydrogen (the back reaction).

In **Chapter 5**, we optimize the reaction conditions for two photocatalysts ($\text{Al}:\text{SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ and $\text{Mg}:\text{SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$) in photocatalytic water splitting. The obtained results indicate that both photocatalysts show a high photocatalytic efficiency and a long-term stability. Detailed exploration of the performance illustrates that catalyst concentration is a very important factor in determining the optimal efficiency of the photocatalysts. These two composite materials obtain their individual optimal photocatalytic gas production rate at different concentration.

In **chapter 6**, recent literature discussing the stability and transients in the active oxidation-state of metal(oxide) nanoparticles co-catalysts in photocatalysis has been summarized. Specifically, the latest insights in the active state of frequently applied co-catalysts systems (Pt, Rh/ Cr_2O_3 and Ni/NiO_x) are

presented. Furthermore, we also show how know-how of other disciplines, such as heterogeneous catalysis or electro-catalysis, and recent advances in analytical methodology, can help to determine the active state of co-catalytic nanoparticles in photocatalytic applications.

In **Chapter 7**, the obtained results in this thesis are summarized and a perspective for photocatalytic water splitting is provided.

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Chapter 2

Transient behavior of Ni/NiO functionalized SrTiO₃ in overall water splitting

Transients in composition of Ni/NiO core/shell co-catalysts deposited on SrTiO₃ are discussed on the basis of state-of-the-art continuous analysis of photocatalytic water-splitting, and *post* XPS and TEM analyses. The formation of excessive hydrogen ($H_2 : O_2 \gg 2$) in the initial stages of illumination demonstrates oxidation of Ni(OH)₂ to NiOOH (Nickel Oxy Hydroxide), the latter catalyzing water oxidation. A disproportionation reaction of Ni and NiOOH, yielding Ni(OH)₂ with residual embedded Ni, occurs when illumination is discontinued, explaining repetitive transients in (excess) hydrogen and oxygen formation when illumination is re-initiated.

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2.1 Introduction

Research on photocatalysis for water-splitting in slurry phase reactors, yielding hydrogen and oxygen, has focused on i) doping, creating optimized semiconductors for conversion of sunlight into excited states (holes and electrons), and ii) functionalizing (doped) semiconductor crystals with so-called co-catalyst nanoparticles to enhance the reaction rates of the necessary surface redox reactions (proton reduction and water oxidation)¹. One of such co-catalyst systems that has attracted significant attention, is a composite of Ni/NiO particles. However, the structure, mode of operation, and stability of the active Ni/NiO particles is yet unresolved, and appears to be dependent on the composition and structure of the semiconductor.²⁻⁷ For strontium titanate (SrTiO₃), a semiconductor capable of inducing both half reactions of overall water splitting, Domen et al² proposed that Ni/NiO core-shell particles provide the catalytic sites for hydrogen evolution. In their proposal, water oxidation is catalyzed by the SrTiO₃ surface. More recently, Osterloh et al.⁷ suggest the core-shell model is not representing the active phase(s), but rather segregated particles of Ni and NiO_x, which promote formation of hydrogen and oxygen, respectively.

Both Domen and Osterloh used batch reactors to evaluate catalytic performance,^{2,7} which complicates evaluation of transients in hydrogen and oxygen evolution during the initial phase of water-splitting. Recently, Crozier et al. reported continuous flow experiments on the use of Ni/NiO core/shell particles to promote activity of TiO₂ or Ta₂O₅ in overall water splitting.^{5,6} During these experiments, oxygen could not be detected and a decreasing trend in hydrogen production rate was observed, which the authors explain on the basis of HRTEM images by oxidation and subsequent dissolution of Ni out of the Ni/NiO core/shell particles. Hollow NiO_x shells were observed, while Ni dissolution was substantiated by ICP analysis of the solution.⁵ Besides the work of Crozier,^{6,5} there has been little research into the transient behavior of functionalized semiconductors in (the initial hours of) photocatalytic activity⁸. Furthermore, transients occurring when the slurry is maintained in dark conditions (catalyst regeneration⁹), to the best of our knowledge, have never been addressed for Ni/NiO core/shell particles.

Therefore, in this study we describe the use of a Continuously Stirred Tank Reactor (CSTR) connected to a micro gas chromatograph equipped with a Pulsed Discharge Detector (PDD), providing unprecedented sensitivity and data density, to analyze the transient behavior of Ni/NiO core/shell particles on SrTiO₃ in the initial stages of water splitting, after preparation and conditioning in the dark. We reveal significant transients in hydrogen production rate, which correlate to changes in the composition and structure of the Ni/NiO core/shell particles. The implications of these transients for determination of the active phase of Ni/NiO core/shell particles on SrTiO₃, as well as the consequences for structural design allowing practical application, are discussed.

2.2 Experimental methods

2.2.1 Preparation of Ni/NiO on SrTiO₃

SrTiO₃ was fabricated *via* a high temperature solid state process^{2,10}. Briefly, stoichiometric amounts of SrCO₃ (99.995 % Sigma-Aldrich) and Rutile TiO₂ (99.995% Sigma-Aldrich) were mixed and calcined at two different temperatures, namely 1000 °C and 1100°C (heating rate 10 K/min), for 10 h. These powders will be referred to as BSTO-1000 and BSTO-1100. Deposition of Ni/NiO core/shell particles on the surface of SrTiO₃ was achieved by a wet impregnation method,² applying a loading amount of 3 wt% NiO. Briefly, 0.2 g SrTiO₃ powder was dispersed in 20 mL of an aqueous solution of 3.95 mM Ni(NO₃)₂. The obtained mixture was stirred for 2 h. Then, the solution was evaporated till dryness at 80 °C overnight, and calcined for 30 min at 400 °C in flowing air (30 mL/min) in a tube furnace. The air above the solid was flushed with N₂ during cooling down to room temperature and then replaced by 5% H₂/N₂ (30 ml/min), followed by reheating the sample to 500 °C (at 10 K/min), and maintaining that temperature for 5 h. The final product was obtained by cooling down in nitrogen flow to 130 °C, and a treatment of 1 h in flowing air (30 ml/min) at this temperature. The Ni/NiO containing samples are labeled BSTO1000-NiO_x and BSTO1100-NiO_x, respectively.

2.2.2 Sample characterization

XRD measurements were performed on a Bruker D2 (Cu $k\alpha$ source) diffractometer. A Nova 600-nanolab HR-SEM (FEI instruments) was used for SEM experiments. TEM imaging of the deposited Ni/NiO particles was performed using a Philips CM300ST-FEG microscope equipped with a Kevex EDX detector. Samples for TEM analysis were prepared by dispersion in ethanol, and deposition onto a carbon coated TEM grid. The X-ray Photoelectron spectroscopy (XPS) measurements were performed on a Quantera SXM (Physical Electronics) instrument, equipped with an Al $K\alpha$ X-ray source (1486.6 eV). The binding energies were referenced to the Ti 2p_{3/2} core level peak at 457.7 eV, since surface carbon quantities were low before and after the photocatalytic experiments.

Reference NiO and NiOOH samples were used to determine the peak positions of the different Ni species in the composite material. Commercial NiO nanopowder from Sigma-Aldrich, (<50 nm particle size, 99.8% trace metals basis) was used. NiOOH was prepared as a thin film on FTO glass, using a three steps electrochemical method previously reported by Chang et al.¹¹

The Ni concentration on samples before and after photocatalytic measurement was determined by Inductively coupled plasma optical emission spectroscopy (ICP-OES), using a Perkin Elmer 8300dv instrument. Ni was dissolved out of various specimens in 4.5 mL of 7M nitric acid.. The Ni loading was determined using results from the isotope with the lowest detection limit.

2.2.3 Photocatalytic activity experiments

The photocatalytic activity of the compounds in pure water was measured using a continuously stirred tank reactor connected to a highly sensitive gas chromatograph (CompactGC Interscience). The GC was equipped with a Pulsed Discharge Detector. The pH of the suspension was measured to be 9 initially, and hardly changed during the experiments. By a constant helium (7N) purge (10 mL/min), the gas to be analyzed was transferred to the GC. In the GC, a 50 μ L sample loop inserted a sample onto a Q-bond column to remove H₂O, and a Molsieve 5A, to separate the gaseous components present in the sample, being

H₂, O₂ and N₂. The optical glass reactor (402.013-OG, Hellma) was illuminated by a 1.5 AM solar simulator (ABET technologies model 10500 low cost solar simulator, 5 cm² beam area), which is representative of the intensity profile of solar radiation. The intensity incident on the reactor window from 300-900 nm amounted to 59 mW/cm², and from 300-400 nm to 0.9 mW/cm². The measurements were performed using 25 mg catalyst in 25 mL of purified water. The apparent quantum efficiency of selected samples was calculated as reported elsewhere¹².

2.3 Results and discussion

SrTiO₃ was prepared according to previous reports. As expected, XRD, Raman spectroscopy and SEM revealed that well-crystallized, phase pure SrTiO₃ particles with an ideal cubic perovskite structure were obtained (see Appendix Figure A2.1-3). Additional diffraction lines at 2θ values of 36.3° and 44.5°, characteristic for Ni and NiO_x (see Appendix Figure A2.1), confirm the loading of well distributed Ni/NiO core/shell particles, as observed in the SEM images of Figure A2.3 (see Appendix).

The activity of the Ni/NiO-SrTiO₃ (BSTO-1000-NiO_x) composite material was tested in overall water splitting under solar light illumination (see Appendix) and the rates of H₂ and O₂ evolution were measured as a function of time (Figure 2.1, Figure A2.4 shows integrated H₂ and O₂ yields). Immediately after starting irradiation, significant H₂ and O₂ production was observed and a maximum H₂ evolution rate of 0.3 μmol min⁻¹ g⁻¹ was obtained after 15 min. Both H₂ and O₂ production rate decline after reaching the maximum, with the O₂ production rate declining significantly faster and approaching apparent steady state conditions. Based on volume and gas-flow rate, CSTR behavior would induce a fast increase in detected products,⁸ whereas the slow transient behavior observed here points towards a composite material that degrades or dynamically changes during photocatalytic testing. Interestingly, significant deviation from the stoichiometric H₂:O₂ ratio of 2:1 was detected. Immediately after switching-off the light, both H₂ and O₂ evolution rapidly discontinued, confirming that H₂ and O₂ are formed in a photo-driven reaction.

Figure 2.1. Transient behavior in H_2 and O_2 evolution during photocatalytic water splitting of 25 mg BSTO-1000- NiO_x (black trace, hydrogen; red trace, oxygen). The light gray and purple areas represent the errors obtained from the standard deviation

Figure 2.2. Transient behavior in H_2 and O_2 evolution during photocatalytic water splitting of 25 mg BSTO-1000- NiO_x (black trace, hydrogen; red trace, oxygen)

To obtain further insights into the transient behavior in the initial phase of photocatalytic water splitting, variable times between illumination and dark conditions were applied. The obtained results are shown in Figure 2.2. The initial transients are in good agreement with the results presented in Figure 2.1. After purging of the reactor with pure He for 1 h in dark conditions, a new maximum (72 % of the initial maximum) in activity of H_2 evolution was obtained, when illumination was re-initiated. Consecutive dark-light cycles

show, that the initial H₂ evolution rate depends on the duration of the dark treatment. After treatment in dark conditions for 48 h, the initial H₂ evolution rate can be fully recovered, although the duration of the transient appears shorter than for the fresh catalyst. The consecutive transient shows again ~73 % of the initial hydrogen activity can be recovered after 1 h in dark conditions. The oxygen evolution rate is significantly larger after keeping the reactor for 48 h in the dark (without reaching a maximum) than obtained for the fresh catalyst, and at the end of the final transient the catalyst is providing a H₂ over O₂ ratio close to 2:1.

This particular behavior clearly points towards a dynamically changing co-catalyst, which has not been previously reported for Ni/NiO. SrTiO₃ is not changing morphology in the course of water splitting, as corroborated by HRSEM and XRD analysis after testing (see Appendix Figure A2.5). The Ni/NiO co-catalyst was characterized after different treatments in order to explain the observed transients. The X-ray photoelectron spectra in the Ni region of the BSTO1000-NiO_x catalyst before illumination, after illumination, and after 48 h dark treatment, are compared in Figure 2.3. For the as-prepared BSTO1000-NiO_x composite a complex Ni peak shape is observed, evidencing that Ni is present in various oxidation states. Deconvolution of the Ni 2p_{3/2} signal confirms the presence of metallic Ni⁰ (at 851.9 eV), Ni²⁺ (as in NiO at 853.5 eV), and Ni²⁺ (as in Ni(OH)₂ at 855.6 eV).^{13–15} The derived relative percentages of Ni metal and Ni oxide, as well as the overall atomic Ni content are shown in Table 1.

Figure 2.3. XPS spectra of the Ni2p_{3/2} region of the BSTO1000-NiO_x sample, i) before illumination NiO_x/STO (as prep.), ii) after illumination NiO_x/STO (meas.), iii) after regeneration (48 h) NiO_x/STO (reg.).

Table 2.1. Relative atomic percentages of Ni⁰ and Ni²⁺ as determined from XPS measurements of the samples at different stages of photocatalytic testing. The Ni loading (at.%) was derived from the total metal loading.

Sample	Ni (at.%)	Ni ⁰ (metallic)	Ni ²⁺ (NiO)	Ni ^{2+/3+} (NiOH) ₂ /NiOOH	Ni ⁰ /Ni ^{2+/3+}
NiO _x /STO (as prep.)	38.8%	12.3%	35.2%	52.5%	0.2
NiO _x /STO (meas.)	21.7%	17.4%	-	82.6%	0.2
NiO _x /STO (reg.)	36.0%	5.7%	-	94.3%	0.06
NiO _x /STO (reg. + tested)	35.0%	8.8%	-	91.2%	0.1

After illumination, the deconvolution of the Ni 2p_{3/2} region suggests that Ni is predominantly present in two different oxidation states, namely Ni⁰ and Ni²⁺ (as in Ni(OH)₂ at 855.6 eV). A contribution of Ni²⁺ in a NiO environment appears less likely, as the width and the symmetry of the Ni signal has clearly changed as compared to the as-prepared composite material. Moreover, it is known from studies on electrochemical oxygen evolution that NiO is not a stable phase^{16,17}. These studies, and thermodynamics (see Pourbaix diagram shown in Figure A2.7), suggest that the formation of NiOOH is feasible upon illumination.^{7,18} Thus, we propose the XPS signature at higher binding energies can be assigned to a mixture of Ni(OH)₂ and NiOOH. Finally, the Ni atomic concentration at the surface of NiO_x/STO(meas.) decreases from 38.8 at% to 21.7 at%, whereas the Ni⁰:Ni^{2+/3+} ratio remains constant at 0.2 (Table 2.1). This apparently decreasing Ni content can be explained by i) leaching of Ni during illumination or ii) particle growth. Leaching can be discarded on the basis of the elemental analysis of the solid and solution after the reaction (see Appendix, Table A2.1 and Table A2.2). In addition, the particle size distributions obtained from SEM before and after the reaction suggest that the decrease in Ni atomic concentration is due to particle growth (see Appendix Figure A2.8).

After regeneration (Ar/dark), the intensity of the Ni-signal at 855.6 is recovered (36 at%). Additionally, the contribution of metallic Ni⁰ (at 851.9 eV) to the Ni signal has almost disappeared (Ni⁰/Ni^{2+/3+} equals 0.06), pointing towards a dynamic restructuring in the dark. Given that the contribution of metallic Ni is significantly smaller than for the sample immediately after reaction, a reaction of NiOOH with metallic Ni (in the core) to form Ni(OH)₂ in dark conditions is proposed:

Finally, when the regenerated sample is illuminated again (see Appendix Figure A2.6), the contribution of metallic Ni slightly increased, while the total Ni loading remained almost constant, pointing towards a now stable configuration of the NiO_x co-catalyst, in agreement with the now close to 2:1 ratio of H₂ over O₂, in the final measurement shown in Figure 2.2.

To further support the results obtained by XPS, HRTEM was used (Figure 2.4 and A2.9 and A2.10). The NiO_x particles in as-prepared BSTO1000- NiO_x (Figure 2.4a) clearly show the core-shell structure (in sizes of about 8-10 nm, with a metallic Ni core of about 6 nm), in agreement with previous reports and XPS data.⁵ The corresponding d-spacing of the lattice fringes obtained from Fast Fourier Transformation (FFT) indicate the presence of metallic Ni (111), and NiO (220). After illumination, i.e. after the first transients shown in Figure 2.2, the structure maintains the core-shell morphology. However, the metallic Ni core appears smaller than in the fresh sample (Figure 2.4b), and the shell appears thicker and to be composed of two separate phases. The d-spacing's derived from the FFT analysis of a variety of NiO_x particles (Figure 2.4b, all d-spacing's are included in Appendix Table A2.3), include values of 6.7–7.7 Å, 2.96 Å and 2.36 Å, which confirms the presence of NiOOH.¹⁹ The additional d-spacing's also indicate the presence of Ni (2.06 Å) and NiO (2.41 Å). Hence, it is reasonable to assume that the shell is composed of NiO with super-positioned NiOOH. The regenerated sample shows different morphologies (Fig. 2.4c). Besides residual core-shell structures, a $\text{Ni}(\text{OH})_2$ phase with small spots of larger contrast embedded in a $\text{Ni}(\text{OH})_2$ layer is apparent, which according to FFT analysis likely consist of metallic Ni (see Appendix Figure A2.9).

Figure 2.4. HRTEM images and corresponding FFT results of the as-prepared (a,d), the illuminated (b,e) and the regenerated (c,f) Ni/NiO-SrTiO₃ composite material. The observed changes in morphology and composition of the Ni/NiO co-catalysts during overall water splitting are also schematically indicated.

The structural changes as identified by XPS and TEM analyses are illustrated in Figure 2.4. In agreement with proposed structures by Domen et al.² and Crozier et al.,^{5,6} the as-prepared co-catalyst is composed of Ni/NiO core/shell particles.^{2,5,6} The NiO phase is transformed by humidity and in aqueous conditions to Ni(OH)₂:²

This Ni/Ni(OH)₂ core/shell particles are not stable under experimental conditions of illumination, and very likely the Ni(OH)₂ phase is oxidized by holes to NiOOH:

In electrochemical water oxidation this is a well-documented process but for Ni/NiO core/shell particles not yet considered.^{16,17} Nevertheless, this reaction might explain the sub-stoichiometric quantity of oxygen formed in the initial transients, and is a sacrificial reaction for highly effective formation of hydrogen in these initial stages.

Predominantly during regeneration, we propose NiOOH disproportionates by reaction with the Ni core (reaction (1)), to form Ni(OH)₂, as previously discussed being in agreement with observed differences in XPS spectra and TEM images. Indeed in electrochemical oxygen evolution it is reported that at potentials below the onset for oxygen evolution (i.e. in the dark), Ni is present as Ni(OH)₂.¹⁷ Reaction (1) is accompanied by vast structural re-arrangement, yielding some remaining Ni embedded in Ni(OH)₂. (Re-)illumination again converts Ni(OH)₂ into NiOOH (hence the initial high hydrogen production rate after a dark period), and dark treatment again converts additional Ni according to reaction (1). As consequence of reactions (1) and (3) the metallic Ni content decreases with time (see XPS) and eventually metallic Ni will only be present in small quantities, if any.

When in close proximity to NiOOH, Ni initially is a sacrificial electron donor (reaction (1)). Our study implies improved performance can be obtained if Ni and Ni(OH)₂ are deposited on separate facets of SrTiO₃, reaction (3) remaining feasible, and reaction (1) being prevented. Osterloh et al.⁷ showed that the

presence of metallic Ni is indispensable for obtaining overall water splitting (catalyzing the hydrogen evolution reaction), while the required amount might be small compared to the amount of NiO_x species, due to very favorable hydrogen evolution kinetics²⁰.

The preparation of well-defined SrTiO₃ crystals providing anisotropic facets was recently reported by Li et al.²¹ Those crystals might be suitable to further improvement of the knowledge of the transient behavior of Ni/NiO SrTiO₃ composite photocatalysts, and the function of the Ni compounds of various oxidation states.

2.4 Conclusions

In conclusion, it is proposed that transients observed upon illumination in hydrogen evolution rates, and corresponding morphological changes of Ni/NiO core-shell particles investigated by TEM, can be explained by in situ formation of NiOOH upon illumination, likely serving as the catalytic entity for water oxidation. The metallic Ni cores serve as sacrificial agent in the water splitting process, and during regeneration. Certainly long term experiments and in-situ studies are required to further explore the dynamic behavior of Ni/NiO core/shell co-catalysts.

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2.7 Appendix

Characterization of SrTiO₃

Figure A2.1. XRD pattern of SrTiO₃ prepared at 1000°C and 1100°C before and after functionalization with Ni/NiO core/shell particles.

Figure A2.2. Raman spectra of a) SrTiO_3 and b) Ni/NiO SrTiO_3 prepared at 1000°C and 1100°C, respectively.

Figure A2.3. High-resolution SEM images of SrTiO₃ prepared at (a,c) 1000°C and (b,d) 1100°C before and after functionalization with Ni/NiO core/shell particles.

Representative high-resolution SEM (HRSEM) images of BSTO1000-NiO_x and BSTO1100-NiO_x catalysts are shown in Figure A2.3. Well-crystallized SrTiO₃ particles with multiple facets can clearly be observed, in particular for the sample prepared at 1100°C. On the surfaces of SrTiO₃ crystallites (most obvious in Figure A2.3d), Ni/NiO particles of variable sizes can be observed. Several Ni/NiO particles are significantly smaller than 10 nm, whereas others are present in the size range of 10-30 nm. The spatial distribution of the particles for BSTO1100-NiO_x is not as homogeneous as for BSTO1000-NiO_x (compare Figure A2.3(c) and A2.3(d)). Some facets appear almost void of particles, whereas others are densely covered, typically containing the Ni/NiO particles of the largest sizes.

Overall water splitting

Figure A2.4. Integrated H₂ and O₂ yields obtained with Ni/NiO core/shell particles deposited on SrTiO₃ prepared at 1000°C and 1100°C, respectively.

To evaluate the photocatalytic activity of the Ni/NiO core/shell functionalized SrTiO₃ materials prepared at different temperatures, solar water splitting under 1.5 AM solar light illumination was performed. As shown in Figure A2.4, H₂ and O₂ evolved simultaneously. BSTO1000-NiO_x outperforms BSTO1100-NiO_x. Thus, for further experiments BSTO1000-NiO_x was used.

Using a measured hydrogen production rate of 0.1 μmol g⁻¹ min⁻¹ (i.e. 6 μmol g⁻¹ h⁻¹), and the determined light intensity of 0.9 mW/cm² in the range of 300-400 nm, the apparent quantum efficiency can be calculated to be 0.6%. Taking the different reaction conditions applied by Osterloh et al¹. into account (in particular the higher light intensity applied), the activity and yield are of the same order of magnitude as reported previously.

Figure A2.5. HRSEM images and XRD pattern of SrTiO₃ after photocatalytic water splitting.

Figure A2.6. XPS spectra of the full Ni_{2p} region of the BSTO1000-NiO_x sample after regeneration for 48 h and additional testing in photocatalytic overall water splitting.

Figure A2.7. Pourbaix diagram of Ni²⁺. The pH of the slurry applied in this study was close to 9.

Table A2.1. Ni loading of the BSTO1000-NiO_x sample before illumination NiO_x/STO (as prep.), after illumination NiO_x/STO (meas.), and Ni concentration in the solution after testing

	Ni loading [wt%]
NiO _x /STO (as prep.)	2.4
NiO _x /STO (meas.)	2.3

Table A2.2. Comparison of Ni leaching during photocatalytic water splitting observed in this study compared with previous work by Crozier et al³.

	sample	Ni loading [μmol]	Ni in solution after testing [μmol]
Crozier et al.	0.2 g TiO ₂ with 1 wt% NiO _x	26.8	4
Our work	30 mg SrTiO ₃ with 3 wt% NiO _x	12.1	0.3

According to ICP analysis, significantly less leaching of Ni occurs from SrTiO₃ (this study) as compared to TiO₂ (Crozier et al³).

Figure A2.8. NiO_x particle size distribution of the as-prepared and the illuminated Ni/NiO.SrTiO₃ composite material.

Table A2.3. d-spacings obtained from FFT analysis of the as-prepared, the illuminated, and the regenerated NiO_x-SrTiO₃ composite materials.

Sample	d-spacing (Å)	Assignment
NiO _x /STO (as prep.)	2.06	Ni
	2.41	NiO
NiO _x /STO (meas.)	6.7	NiOOH
	2.96	
	2.36	
	2.41	NiO
	2.06	Ni
NiO _x /STO (reg.)	4.6	Ni(OH) ₂
	2.6	
	2.1	
	2.46	NiO
	2.06	Ni

Figure A2.9. The FFT analysis (inset) confirms the particle with the larger contrast consists of metallic Ni.

Fresh

Measured

Regenerate

Figure A2.10. HRTEM images of fresh (first row), illuminated (second row), and regenerated (third row) BSTO1000-NiO_x sample.

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Chapter 3

Promoting photocatalytic overall water splitting by controlled Mg incorporation in SrTiO₃ photocatalysts

SrTiO₃ is a well-known photocatalyst inducing overall water splitting when exposed to UV light irradiation of wavelengths < 370 nm. However, the apparent quantum efficiency of SrTiO₃ is typically low, even when functionalized with nanoparticles of Pt or Ni/NiO. Here, we introduce a simple solid state preparation method to control the incorporation of magnesium into the perovskite structure of SrTiO₃. After deposition of appropriate co-catalysts like Pt or Ni/NiO, the photocatalytic water splitting efficiency of the Mg:SrTiO_x composite is up to 20 times higher compared to SrTiO₃ containing similar catalytic nanoparticles, and an apparent quantum yield (AQY) of 10 % can be obtained in the wavelength range of 300 - 400 nm. Detailed characterization of the Mg:SrTiO_x composites revealed that the incorporation of Mg most likely leads to a favorable surface-space-charge layer. This originates from tuning of the donor density of the cubic SrTiO₃ structure by Mg-incorporation and enables high oxygen evolution rates. Nevertheless, interfacing with an appropriate hydrogen evolution catalyst is mandatory and non-trivial to obtain high performance in water splitting.

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3.1 Introduction

Photocatalytic water splitting is an attractive method for storage and conversion of solar energy. However, only few semiconductor materials are capable of driving the overall water splitting reaction^{1,2}. For GaN:ZnO, when modified with Rh/Cr₂O₃ particles, an apparent quantum yield (AQY) of 5.1% (at 410 nm) has been reported^{3,4}. Other effective photocatalysts require excitation by UV light < 300 nm^{5,6}. An AQY of 56% at 270 nm was reported for La-doped NaTaO₃⁵, whereas for Ga₂O₃, AQY of up to 71% have been achieved⁷⁻⁹. Strontium titanate (SrTiO₃) has already been used for almost four decades in photocatalytic water splitting¹⁰⁻¹³, and although progress has been slow in increasing the AQY, SrTiO₃ is among the few examples that actually facilitates overall water splitting under solar-light illumination, besides the aforementioned GaN:ZnO. SrTiO₃ is an ABO₃-type perovskite oxide containing an alkaline-earth-cation on the A site and a tetravalent transient metal cation on the B site¹⁴. For these structures it is usually accepted that introducing new heteroatoms on either an A or B site will lead to changes in 3d electron interactions, eventually tuning the valence state and electronic structure of the perovskite material.^{15,16} For example, through tuning the La³⁺/Sr²⁺ ratio in La_{1-x}Sr_xBO₃ and La_{1-x}Sr_xBO₄ (B = Fe, Co, Mn, or Ni) oxides, Patzke and co-workers¹⁷ demonstrated that even a transition from insulating to metal-like behavior can be achieved. Hence, as a typical perovskite oxide, SrTiO₃ is susceptible to tuning of its chemical and physical properties through altering its composition.^{15,16} Naturally introducing new heteroatoms can also be expected to drastically alter the capabilities of SrTiO₃ in photocatalytic water splitting.

Only recently flux-treatment in SrCl₂ was used to i) improve crystallinity of SrTiO₃, ii) change the particle morphology, and iii) introduce dopants (mainly Al), thereby significantly increasing the apparent quantum yield (@ 360 nm) of to 30%.¹⁸⁻²⁰ At the same time, the same group of researchers reported a similar increase in AQY by simple impregnation of as-prepared SrTiO₃ with various different metal salts and subsequent diffusion of the metal ion into the SrTiO₃ particles by high temperature.¹⁸ Among others, magnesium (Mg) was shown to be a valuable additive, although, as also mentioned by Sakata et al.,¹⁸ a more

detailed understanding of the origin of the enhancement in the overall water splitting performance is required.

Here, a simple two-step solid-state preparation method was applied to incorporate Mg into SrTiO₃. This two-step approach allowed for a well-controlled metal ion incorporation and easy adjustment of the Mg content in the semiconductor material. Thus, a rigorous analysis of the effect of Mg doping on i) the phase purity of SrTiO₃, ii) the properties and effectivity of different co-catalysts and iii) the photocatalytic activity for overall water splitting will be reported. After deposition of an appropriate co-catalyst, such as Pt or Ni/NiO, the photocatalytic overall water splitting (POWS) efficiency is up to 20 times higher compared to the conventional Ni/NiO - SrTiO₃ composite. Furthermore, the obtained results clearly demonstrate the importance of controlling the Mg loading well. In particular, different trends in the overall water splitting activity depending on Mg loading and the applied co-catalyst will be discussed.

3.2 Experimental methods

3.2.1 Materials preparation

Bulk SrTiO₃. Bulk SrTiO₃ was prepared by a well-known high temperature treatment of stoichiometric amounts of SrCO₃ (99.995 % Sigma-Aldrich) and TiO₂ (Rutile phase: 99.995% Sigma-Aldrich).^{21,22} The compounds were thoroughly mixed and subsequently calcined at 1100°C for 10 h.

Mg incorporated SrTiO₃. Mg incorporation into SrTiO₃ was achieved by a two-step high temperature method. First rutile TiO₂ was impregnated with an aqueous MgSO₄ solution using a predefined molar ratio of Mg/Ti. The solution was evaporated to dryness and the powder was calcined in air at 800°C for 2h. Afterwards, the powder was thoroughly rinsed with water afterwards (at least four times), to remove the residual (Mg) sulfate, as verified by Raman spectroscopy (see Appendix Figure A3.1). Then, the obtained MgTiO_x material was mixed with stoichiometric amounts of SrCO₃ and calcined at 1100°C for 10h to obtain targeted products. These materials are referred to as Sr_{1.25}Mg_{0.1}TiO_x, Sr_{1.25}Mg_{0.2}TiO_x, Sr_{1.2}Mg_{0.2}TiO_x, Sr_{1.25}Mg_{0.3}TiO_x, and

$\text{Sr}_{1.25}\text{Mg}_{0.5}\text{TiO}_x$. For comparison, a MgO-loaded SrTiO_3 was prepared by impregnation of the as-prepared bulk SrTiO_3 in an aqueous solution of MgSO_4 (molar ratio of 0.2). After drying, the obtained powder was calcined at 800°C for 2 h in air.

Deposition of Core/Shell Ni/NiO. Modification of the prepared semiconductor materials by core-shell Ni/NiO particles was achieved as previously reported.²² Briefly, 0.2 g of the respective semiconductor powder was dispersed in 20 mL of an aqueous solution of $\text{Ni}(\text{NO}_3)_2$. The obtained mixture was stirred for 2 h, subsequently, the solution was evaporated at 80°C overnight, and finally the obtained powder was calcined for 1 h at 400°C in a tube furnace (30 mL/min synthetic air; heating rate 10 K/min). After cooling down to room temperature in N_2 , the material was reduced for 10 h at 500°C in a gas mixture of 5% H_2/N_2 (heating rate 10 K/min; flow 80 mL/min). The final product was obtained by cooling down in nitrogen flow to 130°C , and a treatment of 1 h in flowing air (30 mL/min) at this temperature.

Deposition of Pt. Photodeposition was applied to deposit Pt nanoparticles on the surface of Mg-modified SrTiO_x . Typically, 0.2 g of the prepared material was dispersed into 20 mL of H_2PtCl_6 solution and then illuminated under UV light (360-380 nm, $3.21\text{ mW}/\text{cm}^2$) for 5 h. Afterwards the powder was centrifuged and dried under 80°C for overnight.

3.2.2 Sample characterization

XRD measurements were performed on a Bruker D2 (Cu K_α source) diffractometer. The phase composition of the different materials was obtained using the Highscore Plus software. Raman spectroscopy (Bruker Senterra) was performed at room temperature with a 532 nm green laser (2 mW). A Philips PW 1480 was used for XRF analysis. UV-Vis diffuse reflectance spectra (DRS) were recorded with a UV-Vis spectrophotometer (Thermo Scientific, Evolution 600), the reflectance data were converted to Kubelka-Munk plots and the corresponding Tauc plots. A Nova 600-nanolab HR-SEM (FEI instruments) was used for SEM experiments. Mott-Schottky measurements were conducted in a three electrode setup (using a Biologic VSP Potentiostat) using aerated 0.5 M Na_2SO_4 as the electrolyte. Photoelectrochemical measurements were performed

in degassed 0.5 M Na₂SO₄ + Na₂SO₃ (pH = 7.1). A Xe lamp with AM1.5G filter was used as light source an intensity of 1.5 suns using back side illumination. The Mg-modified SrTiO_x working electrode was prepared by electrophoretic deposition of the corresponding powder on an FTO substrate.²³ Briefly, electrophoretic deposition was carried in a two-electrode configuration in acetone solution (10 mL) with 15 mg iodine dissolved in the solution. By applying a bias of 40 V for 3 minutes between the FTO substrate and a Pt electrode, the powder was deposited.

3.2.3 Photocatalytic activity experiments

The photocatalytic activity of the compounds was measured using a continuously stirred tank (CSTR) reactor connected to a highly sensitive gas chromatograph (CompactGC Interscience). The GC was equipped with a Pulsed Discharge Detector (PDD). By a constant helium (7N) purge (10 mL/min; in these conditions back-reaction of H₂ and O₂ is limited/suppressed due to the low H₂ and O₂ partial pressures), the gas to be analyzed was transferred to the GC. In the GC, a 50 µL sample loop inserted a sample onto a Q-bond column to remove H₂O, and a Molsieve 5A to separate the gaseous components present in the sample (H₂, O₂ and N₂). The optical glass reactor (402.013-OG, Hellma) was illuminated by a 1.5 AM solar simulator (ABET technologies model 10500 low cost solar simulator, 4.9 cm² beam area), which is representative of the intensity profile of solar radiation (see Appendix Figure A3.13). The incident intensity on the reactor window from 300-900 nm amounted to 59 mW/cm², and from 300-400 nm amounted to 0.9 mW/cm². The measurements were performed using 25 mg catalyst in 25 mL of ultrapure water. After immersion of the photocatalyst, the pH of the solution was measured to be 9. Half reaction measurements were performed with the unmodified Mg:SrTiO_x materials (no co-catalyst) by adding the corresponding sacrificial agents (2 mM FeSO₄ for H₂ evolution and 2 mM Fe₂(SO₄)₃ for O₂ evolution) to the prepared photocatalyst slurry solution.

3.3 Results and discussion

3.3.1 Structural characterization of Mg-modified SrTiO₃

Mg-modified SrTiO₃ was prepared by a two-step synthesis. After impregnation of rutile TiO₂ with MgSO₄ and subsequent annealing, the obtained powder was converted into Mg:SrTiO₃ by high temperature treatment using SrCO₃ as strontium source. The composition of the different Mg-modified SrTiO₃ materials was first verified by X-ray fluorescence (XRF), yielding the atomic ratios provide in Table 3.1.

Table 3.1. Analysis of the Mg content and phase composition of Mg:SrTiO _x materials.		
Sr _x (Mg _y Ti)O	Composition (by XRF)	Phase composition (by XRD)
For $x = y + 1$	$\text{Sr}_{1.2}\text{Mg}_{0.2}\text{TiO}_x$ $\text{Sr}_{1.25}\text{Mg}_{0.3}\text{TiO}_x$	Pure cubic (Mg:)SrTiO ₃ phase
For $x > y + 1$	$\text{Sr}_{1.25}\text{Mg}_{0.1}\text{TiO}_x$ $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$	Sr ₂ TiO ₄ (8-40%) + (Mg:)SrTiO ₃ (60-92%) composite
For $x < y + 1$	$\text{Sr}_{1.25}\text{Mg}_{0.5}\text{TiO}_x$	Rutile TiO ₂ (20%) + (Mg:)SrTiO ₃ (80%) composite

Structural analysis of the samples performed by X-ray diffraction (XRD) and Raman spectroscopy is shown in Figure 3.1. The main diffraction lines of all samples (Figure 3.1a), independently of the Mg-content, can be assigned to cubic SrTiO₃ with orientations of (110), (111), (200), (211) and (220) located at 2θ of 32.58°, 40.1°, 46.61°, 57.9° and 67.95°, respectively.²⁴ The XRD pattern of Sr_{1.25}Mg_{0.3}TiO_x indicates that a phase-pure cubic SrTiO₃-like material was obtained. Generally, the FWHM of the (110) diffraction line hardly changes. From the FWHM of the (110) diffraction line of 0.19-0.36, primary crystal size ranges were estimated to range from 10-20 nm. For non-stoichiometric ratios of (Mg+Ti):Sr < 1, as in Sr_{1.25}Mg_{0.1}TiO_x and Sr_{1.25}Mg_{0.2}TiO_x, diffraction lines at 31.6° and 43.9° are observed, which can be assigned to the tetragonal Sr₂TiO₄ phase.²⁵ Alternatively, for samples exceeding the stoichiometric ratio ((Mg+Ti):Sr > 1), non-converted rutile TiO₂ is observed, in addition to cubic SrTiO₃.

Figure 3.1. a) XRD patterns and b) Raman spectra of Mg-modified SrTiO₃ with different Mg-loadings. Contributions of the SrTiO₃ phase (filled square), Sr₂TiO₄ phase (filled triangle), and TiO₂ phase (filled circle) are indicated in each figure.

To further explore structural changes induced by Mg-incorporation into SrTiO₃, Raman spectroscopy was employed (Figure 3.1b). Comparison with measured reference spectra of tetragonal Sr₂TiO₄ and rutile TiO₂ (see Appendix Figure A3.1) validate that Raman assignment are in agreement with phase identification by XRD. Only for materials with near stoichiometric molar ratios of (Mg+Ti):Sr, the typical second order broad bands at 200-400 cm⁻¹ and 600-800 cm⁻¹ for SrTiO₃ in its cubic structure are obtained,^{25,26} whereas Sr₂TiO₄ or Rutile TiO₂ can be clearly identified in Raman spectra of non-stoichiometric compositions.

For comparison, MgO-loaded SrTiO₃ was prepared by impregnation of as-prepared SrTiO₃ with MgSO₄. In contrast to the Mg-modified SrTiO₃ materials, the diffraction lines of SrTiO₃ are dominant, and only the characteristic Raman bands of SrTiO₃ are observed (see Appendix Figure A3.2), indicating that on-surface deposited MgO did not alter the cubic structure of SrTiO₃. The normalized intensities above 1000 cm⁻¹ are likely owed to residual sulphate in this sample (see Appendix Figure A3.1).

High-resolution SEM (Figure 3.2) and DRS (see Appendix Figure A3.3) were applied to investigate the morphology and the optical properties, i.e. the band gap of the prepared Mg-modified SrTiO₃ materials. In agreement with XRD and Raman spectroscopy, similar particle morphologies, e.g. crystals with multiple

facets were observed for phase pure Mg:SrTiO₃. For composite structures such as Sr_{1.25}Mg_{0.2}TiO_x consisting of SrTiO₃ and Sr₂TiO₄ phases, particles with smooth extended facets are observed. Likewise, using Tauc plots a slightly larger indirect band gap is estimated for mixed phase Mg-modified SrTiO_x materials (3.2 eV), compared to the pure phase sample Sr_{1.25}Mg_{0.3}TiO_x (band gap of 3.1 eV) which is in agreement with the generally larger band gap of Sr₂TiO₄ (Figure A3.3b).

Figure 3.2. HRSEM images of Mg:SrTiO_x with Ni/NiO co-catalyst and different Mg-content: (a) Sr_{1.25}Mg_{0.3}TiO_x, (b) Sr_{1.2}Mg_{0.2}TiO_x, (c) Sr_{1.25}Mg_{0.2}TiO_x, (d) MgTiO_x/SrTiO₃

3.3.2 Overall water splitting performance

Figure 3.3. Photocatalytic performance in H₂ and O₂ evolution under solar light. (a) Optimization of NiO_x loading for SrTiO₃ and Sr_{1.25}Mg_{0.2}TiO_x, (b) Comparison of the photocatalytic transient of Ni/NiO-modified Sr_{1.25}Mg_{0.2}TiO_x and unmodified Sr_{1.25}Mg_{0.2}TiO_x. Time-intervals to determine the peak, and steady-state rates in hydrogen and oxygen production are highlighted.

The photocatalytic activity of the prepared materials was tested after applying suitable co-catalysts. Here, Pt and Ni/NiO core-shell structures were used, since these co-catalysts have previously been reported to facilitate photocatalytic overall water splitting (POWS) of SrTiO₃.^{21,22} The Ni/NiO loading was found to be optimal at 1 wt% for SrTiO₃ and Sr_{1.25}Mg_{0.2}TiO_x (Figure 3.3a). Hence, all Mg-modified SrTiO_x materials were modified with the optimized Ni/NiO loading of 1 wt% and subsequently tested in overall water splitting in a continuously stirred tank reactor (CSTR) under solar light illumination. The evolution rates of H₂ and O₂ were measured with a micro gas chromatograph equipped with a Pulsed Discharge Detector (PDD). Here, all measurements were performed with a purge-gas flow rate of 10 ml/min. It should be noted that the back reaction of H₂ and O₂ to water might be suppressed by the flow of the purge gas, and optimization of the purge gas flow could lead to complete prevention of this back reaction.²⁷ We currently evaluate the effect of purge-gas rate, light intensity, reactor geometry, and catalyst concentration on the performance of our photocatalytic flow reactor in water splitting and oxidation of H₂ to H₂O.

As previously shown for Ni/NiO-modified SrTiO₃,²² transients in H₂ and O₂ evolution are observed for all Mg-modified SrTiO₃ materials. Typical transient evolution curves for hydrogen and oxygen obtained with Ni/NiO-modified Sr_{1.25}Mg_{0.3}TiO_x are shown in Figure 3.3b (for further information about the transient evolution of H₂ and O₂ with the other Mg-modified SrTiO₃, as well as different reference materials see Appendix Figure A3.4 and A3.5). Thus, for Ni/NiO-modified Sr_{1.25}Mg_{0.2}TiO_x, a peak in both H₂ and O₂ evolution rate was obtained after 30 min of testing, and only after three hours of continuous testing, close to steady state, catalytic evolution rates of hydrogen and oxygen were measured. We tentatively assign the transients to changes in the Ni/NiO structure and presumably the oxidation states of Ni, which is in agreement with our recent results for Ni/NiO-modified SrTiO₃.²²

Although the transient behavior of the Ni/NiO co-catalysts has to be further explored (see Appendix Figure A3.5), a clear improvement in the POWS after Mg modification of SrTiO₃ is obtained. Peak efficiencies as well as steady-state rates suggest that a small Mg-content drastically improves the performance of the composite photocatalysts. Furthermore, the photocatalytic data reveal that the highest POWS are obtained for materials with a fully maintained SrTiO₃ phase (Figure 3.4). For the Ni/NiO-modified Sr_{1.25}Mg_{0.3}TiO_x photocatalyst, H₂ peak and steady-state efficiencies of 8.8 μmol·g⁻¹·min⁻¹ and 1.2 μmol·g⁻¹·min⁻¹ are obtained, respectively, resulting in a state-of-the-art apparent quantum efficiency of 9.1 % in steady-state conditions, at a ratio of H₂ and O₂ close to 2:1 (since Mg:SrTiO₃ is absorbing light below 400 nm, we estimated the apparent quantum yield using intensities in the wavelength range of 300 - 400 nm as emitted by the solar simulator; see Appendix Figure A3.6 for further information). In comparison to Ni/NiO-SrTiO₃ and Ni/NiO-modified MgO-loaded SrTiO₃, a 20 times higher steady-state efficiency is obtained (Figure 3.4a). Here, it should be noted that the reported transients for Ni/NiO-SrTiO₃ and Ni/NiO-modified MgO-loaded SrTiO_x can only be visualized due to the time resolution of our micro-GC, and sensitivity towards H₂ and O₂ provided by the PDD-detector. Usually these initial changes in the H₂ and O₂ evolution rates are not observed when using batch reactors connected to GCs with TCD detectors, typically allowing the first measurement only after 1 hour of

illumination. Our future work is dedicated to stabilizing the initial rates induced by the Ni/NiO-Mg:SrTiO_x composites.

For samples with high Mg-loadings, such as in Sr_{1.25}Mg_{0.5}TiO_x, the performance drastically lower (Figure 3.4a). The photocatalytic performance of pure Sr₂TiO₄, Mg_{0.2}TiO_x, and mixtures of Sr₂TiO₄/SrTiO₃ is also low and none of these samples show a comparable activity to the Mg:SrTiO₃ photocatalysts (see Appendix Figure A3.7). We therefore exclude possible effects of novel phases and conclude that Sr₂TiO₄ and Mg_{0.2}TiO_x are inactive phases for POWS.

Figure 3.4. Photocatalytic efficiency in H₂ and O₂ evolution under solar light. (a) photocatalytic behavior different Mg ratio with 1 wt% NiO_x modification, (b) Photocatalytic half reaction with sacrificial agent (2 mM FeSO₄ for H₂ evolution and 2 mM Fe₂(SO₄)₃ for O₂ evolution).

Table 3.2. Photocatalytic water splitting performance of the various Mg-modified SrTiO_x with Ni@NiO or Pt co-catalysts.

Sample	Co-catalyst	H ₂ (nmol min ⁻¹)	O ₂ (nmol min ⁻¹)
SrTiO ₃	1 wt% Ni/NiO	1.8. ^a / 3.8 ^b	0.251 ^a / 0.8 ^b
Mg _{0.1} Sr _{1.25} TiO _x	1 wt% Ni/NiO	18 ^a / 60.8 ^b	9.5 ^a / 32.8 ^b
Mg _{0.2} Sr _{1.25} TiO _x	1 wt% Ni/NiO	21.8 ^a / 57.8 ^b	12.5 ^a / 35.8 ^b
Mg _{0.3} Sr _{1.25} TiO _x	1 wt% Ni/NiO	39.8 ^a / 220.3 ^b	22.8 ^a / 113 ^b
Mg _{0.5} Sr _{1.25} TiO _x	1 wt% Ni/NiO	0.5 ^a / 0.63 ^b	0.18 ^a / 2 ^b
SrTiO ₃	0.5 wt% Pt	0.5	0.3
Mg _{0.1} Sr _{1.25} TiO _x	0.5 wt% Pt	10.8	6.3
Mg _{0.2} Sr _{1.25} TiO _x	0.5 wt% Pt	7.8	4.3
Mg _{0.3} Sr _{1.25} TiO _x	0.5 wt% Pt	0.5	1.3
Mg _{0.5} Sr _{1.25} TiO _x	0.5 wt% Pt	0.005	0.5
[a] steady state rate; [b] peak rate			

As for Ni/NiO-modified composite materials, significantly higher POWS were obtained for Mg-modified SrTiO₃ materials compared to bare SrTiO₃ photocatalysts after photodeposition of 0.5 wt% Pt (Table 3.2 and Figure A3.8-A11). In contrast to the Ni/NiO-modified composite materials, however, steady-state rates were obtained within a short time period of solar illumination. Again, the samples with relatively high Mg content performed significantly worse compared to those of low Mg content, and the mixed-phase Mg_{0.1}Sr_{1.25}TiO_x catalyst showed the highest POWS activity. After Pt deposition, grey powders of SrTiO₃ and Mg_{0.1}Sr_{1.25}TiO_x were obtained (see Appendix Figure A3.12), as expected for materials with metallic Pt, whereas the other samples with higher Mg content were slightly yellow, evidencing the deposition of Pt in a higher oxidation state.²¹

To evaluate the surface reactivity of Mg:SrTiO_x, we tested the efficiency of the materials for H₂ and O₂ evolution using sacrificial agents (Figure 3.4b), namely FeSO₄ and Fe₂(SO₄)₃. As shown in Figure 4b, the presence of Mg in the SrTiO₃ structure has a strong influence on the water oxidation activity, and the

measured oxygen evolution rates follow the trends observed for Mg-modified SrTiO_x with Ni/NiO co-catalysts in overall water splitting. Indeed, the oxygen evolution rates closely resemble the measured peak efficiencies with Ni/NiO-Sr_{1.25}Mg_{0.3}TiO_x. For proton reduction to hydrogen, however, Mg:SrTiO_x shows little activity, indicating that Pt or Ni/NiO are necessary for this half reaction. Based on all our observations, we conclude that phase pure, cubic Mg:SrTiO_x is a favorable material for POWS. The activity is likely owed to the beneficial influence of Mg on the electronic structure of SrTiO₃, combined with high catalytic activity for O₂ evolution, whereas a suitable hydrogen evolution catalyst is required for high performance in POWS.

3.3.3 Mg modification: Effects on the electronic structure

Figure 3.5. Photoelectrochemical performance of SrTiO₃ and Mg:SrTiO_x samples in 0.1 M KPi + 1 M Na₂SO₃ (pH = 7.1) using 1.5 sun illumination.

To better understand the band structure and charge separation of Mg-modified SrTiO_x, photoelectrochemical measurements and Mott-Schottky analysis were applied on the Mg:SrTiO_x composites (without co-catalyst, Figure 3.5 and Figure 3.6). Photoelectrochemical characterization of the phase pure Mg:SrTiO_x and unmodified SrTiO₃ were performed after immobilization by electrophoretic deposition on FTO substrates. As shown in Figure 3.5, both materials exhibit the characteristic light response of n-type semiconductor materials. In addition,

a cathodic shift of the photocurrent onset potential can be observed as indicated by the increased light response at negative potentials, which suggests that the band structure has been changed through Mg incorporation. In this case, Mott-Schottky analysis was further conducted to understand the differences in electronic structure between Mg:SrTiO_x composites and unmodified SrTiO₃.

Using the following Mott-Schottky relation (eqn. 1)

$$\frac{1}{C_{sc}^2} = \frac{2}{e\epsilon\epsilon_0 N} \left(E_{appl} - E_{fb} - \frac{KT}{e} \right) \quad (1)$$

where C_{sc} is the capacitance of space charge layer, e is the charge of the electron, ϵ is the dielectric constant of semiconductor (300 for SrTiO₃^{28,29}), ϵ_0 is the vacuum permittivity of free space, N is the donor density (electron donor concentration for an n -type semiconductor or hole acceptor concentration for an p -type semiconductor), E_{appl} is the applied potential, E_{fb} is the flat band, K is the Boltzmann constant, and T is the absolute temperature. The flat band positions (E_{fb}) and donor intensity (N) were calculated and are summarized in Table 3.^{10,11} Additionally, the conduction band position (E_{CB}) and the depletion layer thickness (W_o) obtained by eqn. 2 and eqn. 3 are summarized.

$$E_{CB} = E_{fb} + \frac{KT}{e} \ln \left(\frac{N}{N_c} \right) \quad (2)$$

$$W_o = \left(\frac{2\epsilon\epsilon_0}{eN} \right)^{1/2} \quad (3)$$

where N_c is the effective density of states in the conduction band, which is roughly estimated to be $2.8 \times 10^{20} \text{ cm}^{-3}$ for SrTiO₃.³⁰

Figure 3.6. Mott-Schottky curves of Mg:SrTiO_x with different Mg-loadings obtained at 2.5 kHz in 0.5 M Na₂SO₄.

Table 3.3. Summary of the obtained Mott-Schottky results for SrTiO₃ and Mg: SrTiO_x materials with different Mg-content.

Sample	E_{fb} (V _{RHE})	E_{CB} (V _{RHE})	N (cm ⁻³)	W_o (nm)
SrTiO ₃	-0.25	-0.3	4.82×10^{19}	26
Mg _{0.1} Sr _{1.25} TiO _x	-0.31	-0.39	1.27×10^{19}	51
Mg _{0.2} Sr _{1.25} TiO _x	-0.33	-0.41	1.26×10^{19}	51
Mg _{0.3} Sr _{1.25} TiO _x	-0.34	-0.41	1.61×10^{19}	45

While generally in agreement with previous reports,¹² the Mott-Schottky analysis reveals that the donor density of Mg:SrTiO_x is significantly lower compared to the unmodified SrTiO₃ sample, which is in good agreement with earlier impedance measurements on Ho-modified SrTiO₃ photoelectrodes and first principle calculations on Mg-modified TiO₂ hollow spheres.^{31,32} The slight increase in donor density observed for the phase-pure Mg_{0.3}Sr_{1.25}TiO_x might be

related to the Sr_2TiO_4 phases present in the $\text{Mg}_{0.1}\text{Sr}_{1.25}\text{TiO}_x$ and $\text{Mg}_{0.2}\text{Sr}_{1.25}\text{TiO}_x$ materials. Furthermore, the calculations suggest that the conduction band position is moved slightly upwards to more negative potentials and that the depletion layer thickness is increasing. For a wide band gap semiconductor, the depletion layer thickness (W_0) is of major importance, as this determines surface-confined effective charge separation, and hence improves light utilization (Scheme 3.1).

Scheme 3.1. Schematic summary of the effect of Mg incorporation into SrTiO_3 on the electronic structure of the synthesised materials.

Thus, for a depletion layer thickness equal to the penetration depth of the incident light, maximum photocatalytic efficiencies can be expected.^{33–35} It should be noted that in contrast to other studies where by Mg-modification an intrinsically n-type doped material was converted into a p-type semiconductor,^{36,37} all samples prepared in this study demonstrate n-type behavior (Figure 3.6). Electrodes prepared from powdered materials are far from ideal for Mott-Schottky analysis and certainly a systematic impedance analysis using more comprehensive models and better defined $\text{Mg}:\text{SrTiO}_x$ films are indispensable to use the full potential of the Mott-Schottky analysis. Nonetheless, the Mott-Schottky and PEC analysis (Figure 3.5) are in good agreement with the catalytic data shown for the Ni/NiO and Pt-modified materials. The improved performance can likely be assigned to a favorable

(surface) electronic structure of the Mg-modified SrTiO_x materials and to a cathodic shift of the E_{fb} associated with a larger space charge layer.

It is expected that further increases in POWS can be achieved by slightly modifying the donor density, however, special care has to be taken when modifying the obtained materials with the required co-catalysts. Based on the results obtained with Ni/NiO co-catalysts, the highest POWS can be achieved with the phase-pure Mg_{0.3}Sr_{1.25}TiO_x. For Pt-modified samples with increasing Mg-content a similar trend is observed. However, the phase-pure Mg_{0.3}Sr_{1.25}TiO_x sample is hardly active, evidencing that the interface between the photodeposited Pt particles is not favorable and/or that Pt is present in an oxidized state; the oxide being less suitable to drive the H₂ evolution reaction. In the presence of HER active metallic Pt nanoparticles (even trace amounts might be sufficient^{38,39}), we expect a similar activity increase, as observed for the Ni/NiO-modified Mg_{0.3}Sr_{1.25}TiO_x composite. Future studies will be mainly focused on stabilizing the high initial (peak) activity of the Ni/NiO-modified phase pure Mg_{0.3}Sr_{1.25}TiO_x material and the development of alternative co-catalysts providing long-term stability during POWS.⁴⁰

3.4 Conclusions

In this study, a simple solid state method was applied to prepare Mg-modified SrTiO_x photocatalysts. As shown by structural characterization, variation of Mg-content results in the synthesis of materials consisting of various phases. Only for a stoichiometric ration of (Mg+Ti):Sr, phase pure cubic SrTiO₃ materials were obtained. After deposition of suitable co-catalysts, like Ni/NiO or Pt, the synthesized materials showed dramatic improvement in the photocatalytic overall water splitting (POWS) rates compared to unmodified SrTiO₃. Among all the Mg-modified SrTiO_x samples tested, the phase pure material Sr_{1.25}Mg_{0.3}TiO_x, provided the highest steady-state apparent quantum yield of 9.1% using solar light illumination (300-400 nm). Any effect of the phases present in minor quantities on the POWS were ruled out by a series of reference measurements. Using Mott-Schottky measurements and photocatalytic test reactions with sacrificial agents, the beneficial effect of Mg

is assigned to extension of the depletion layer (from 25 to 50 nm), allowing for better oxygen evolution capabilities of the Mg-modified SrTiO_x materials. On the other hand electron transfer to the surface is limited and an appropriate interface with a hydrogen evolution catalysts needs to be formed to drive the overall water splitting reaction. Among the co-catalysts tested Ni/NiO, in an optimized Ni/NiO -loading of 1 wt%, seems to be better suited than Pt.

3.5 Acknowledgements

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3.7 Appendix

Characterization of Mg:SrTiO_x

Figure A3.1. (a) Raman Characterization of Sr_2TiO_4 and $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$, (b) Raman Characterization of Mg doped SrTiO_3 , (c) Raman Characterization of Mg: SrTiO_x and Rutile TiO_2 , (d) Raman Characterization of SrTiO_3 and MgO loaded SrTiO_3 .

Figure A3.2. XRD pattern of SrTiO_3 and MgO loaded SrTiO_3

Figure A3.3. Tauc plot of unmodified Mg:SrTiO_x and Ni/NiO deposited Mg:SrTiO_x

Photocatalytic measurements

Figure A3.4. Photocatalytic H₂ and O₂ evolution rates under solar light for various Mg:SrTiO_x materials. All samples were modified with 1wt% Ni/NiO as co-catalyst by conventional impregnation .

To investigate the influence of Mg on the performance of the applied Ni/NiO co-catalyst unmodified (no Mg-incorporation into the structure) SrTiO₃ Mg was introduced into the impregnation step with Ni to obtain a series of Mg-modified Ni/NiO co-catalysts. The performance of the obtained materials is shown in Fig. A3.6 (only H₂ evolution rates). While certainly a difference in the transient behavior compared with Ni/NiO-modified SrTiO₃ materials is observed none of the Mg-modified Ni/NiO samples shows similar performances to the Mg-modified SrTiO_x materials. Thus, we attributed the observed increase in H₂ and O₂ evolution rate (Figure A3.4) to the intrinsic materials properties of Mg-modified SrTiO_x.

Figure A3.5. Photocatalytic behaviour in H₂ and O₂ evolution under solar light for 3wt% Ni/NiO modified Mg:SrTiO_x.

The apparent quantum yield (AQY) reported here is determined in agreement with the definition of the external quantum yield and is defined as the ratio of two times the rate of collection of H₂ (mol H₂ s⁻¹) to the incident photon rate (I₀(λ) in Einstein s⁻¹).

$$AQY = \frac{2 \text{ rate of collection of H}_2}{I_0(\lambda)} \times 100$$

The integrated photon flux is = $1.404 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}$.

The illuminated area is 4.9 cm² and the incident photon rate is thus I₀(λ) = $1.14 \times 10^{-8} \text{ mol s}^{-1}$

Figure A3.6. Apparent quantum yield measured for the different NiO_x modified $\text{Mg}:\text{SrTiO}_x$ materials in close to steady-state conditions. Error bars shown in this figure were obtained by the standard deviation from at least three measurements .

Figure A3.7. (a) Comparison of Photocatalytic transient with $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO_x and Sr_2TiO_4 -1% Ni/NiO_x , (b) Comparison of Photocatalytic transient with $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO_x and $\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO_x , (c) Comparison of Photocatalytic transient with $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO_x and SrTiO_3 -1% Ni/NiO_x , (d) Comparison of Photocatalytic transient with $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO_x and $\text{SrTiO}_3/\text{Sr}_2\text{TiO}_4$ -1% Ni/NiO_x .

Figure A3.8. (a) Comparison of Photocatalytic transient with $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$ -1%Ni/NiO and Sr_2TiO_4 -1%Ni/NiO, (b) Comparison of Photocatalytic transient with $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO and $\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO, (c) Comparison of Photocatalytic transient with $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO and SrTiO_3 -1% Ni/NiO, (d) Comparison of Photocatalytic transient with $\text{Sr}_{1.25}\text{Mg}_{0.2}\text{TiO}_x$ -1% Ni/NiO and $\text{SrTiO}_3/\text{Sr}_2\text{TiO}_4$ -1% Ni/NiO

Figure A3.9. Photocatalytic behavior in H_2 and O_2 evolution under solar light for 0.5 wt% Pt functionalized Mg:SrTiO_x .

Figure A3.10. Photocatalytic steady state efficiency in H₂ and O₂ evolution of Pt functionalized Mg:SrTiO_x catalysts.

Figure A3.11. Photocatalytic H₂ evolution of Mg:SrTiO_x-0.5% Pt in 2 mM FeSO₄.

Figure A3.12. Pt-modified Mg:SrTiO_x materials. Distinct changes in sample colour are observed with increasing Mg-content in the Mg:SrTiO_x samples.

Figure A3.13. The intensity incident on the reactor window from 300-900 nm amounted to 59 mW/cm², and from 300-400 nm to 0.9 mW/cm²

Chapter 4

Effect of Cr_2O_3 on Performance of Ni/NiO-Mg:SrTiO₃ in Photocatalytic Water Splitting

The dynamic features of Ni/NiO-SrTiO₃ and Ni/NiO-Mg:SrTiO₃ in photocatalytic water splitting have been intensively discussed in Chapters 2 and 3. Changes in oxidation state and morphology of Ni/NiO induce decreasing performance of the catalyst formulation. Here, we show that photodeposition of Cr_2O_3 on the Ni/NiO-Mg:SrTiO₃ composite drastically enhances the performance. An apparent quantum efficiency of 30% is achieved under 365 nm LED illumination, which is maintained for a period of at least 70 hours. By advanced ICP measurements, we demonstrate that deposition of Cr_2O_3 prevents leaching of Mg- and Ni-ions into the solution. The tentative reasons behind this observation are discussed.

4.1 Introduction

Metal oxides and the corresponding metal nitrides in d^0 and d^{10} configuration show promising activity in the photocatalytic overall water splitting reaction (POWS). Frequently investigated materials include TiO_2 ¹⁻³, SrTiO_3 ⁴⁻⁶, NaTaO_3 ^{7,8}, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ^{9,10}. Co-catalysts are usually necessary to obtain high efficiency in charge transfer and to improve the kinetics of surface reactions. In previous chapters, the performance of core/shell-structured Ni/NiO has been addressed, as well as the dynamics changes that have been observed during POWS¹¹. We demonstrated that the photo-generated holes of SrTiO_3 oxidize NiO to NiOOH during illumination, resulting in an excess of H_2 evolution. However, the stability of core/shell Ni/NiO limits its application in long term photocatalytic reactions. Furthermore, Crozier¹² and co-workers investigated the structural evolution of core/shell Ni/NiO particles on TiO_2 during POWS, and they observed significant leaching of Ni, leaving empty NiO-shells.

Recently, combining Cr_2O_3 with various transition metals (e.g. Rh, Ni, or Ru)¹³ to form a metal (oxides)/ Cr_2O_3 core/shell type co-catalyst has been shown to induce remarkable improvement in photocatalytic activity of the previously mentioned semiconductors, and in particular SrTiO_3 . It is reported¹⁴ that Cr_2O_3 allows diffusion of protons through the shell while inhibiting O_2 to penetrate and reach the metal surface, thus preventing the back reaction (dark reaction - $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$). Besides the synthesis of core/shell type particles, co-impregnation of CrO_x and other transition metals, generating mixed oxide nanoparticles¹⁵, has also been successfully employed to improve the photocatalytic efficiency.

In the present study Cr_2O_3 is deposited on the Ni/NiO-Mg:SrTiO₃ composite¹⁶ by a photodeposition procedure. Photodeposition of Cr_2O_3 on the Ni/NiO-Mg:SrTiO₃ composite significantly improves the photocatalytic activity and stability. TEM-EDX and ICP-OES confirm Cr_2O_3 prevents leaching of various elements of the catalytic formulation, and the origin of this observation is discussed.

4.2 Experimental section

4.2.1 Material preparation

Bulk SrTiO₃. Briefly, stoichiometric amounts of SrCO₃ (99.995 % Sigma-Aldrich) and Rutile TiO₂ (99.995% Sigma-Aldrich) were mixed and calcined at 1100 °C for 10 h.

Mg:SrTiO₃. Typically, two steps were applied in the procedure. First, MgSO₄ was mixed with Rutile (TiO₂) and treated at 800 °C, followed by mixing with SrCO₃ and calcination at 1100 °C for 10 hours. The details of the procedure are described chapter 4, and only pure phase Sr_{1.25}Mg_{0.3}TiO_x was used in this chapter 5, named as Mg:SrTiO₃.

Deposition of Core/Shell Ni/NiO. Briefly, 0.2 g Mg:SrTiO₃ powder was dispersed in 20 mL of an aqueous solution of Ni(NO₃)₂. The obtained mixture was stirred for 2 h and the solution evaporated till dryness at 80 °C overnight. The Ni-precursor was converted to NiO at 400 °C in flowing air (30 mL/min) in a tube furnace, followed by treatment in 5% H₂/N₂ (80 ml/min) at 500 °C (at 10 K/min) for 10 h. Core/Shell Ni/NiO was obtained by treatment at 130 °C of 1 h in flowing air (30 ml/min). The Ni loading was verified to be 1 wt%.

Cr₂O₃ deposition. In short, 0.1g Ni/NiO-Mg:SrTiO₃ was dispersed into 10 mL of a 10 mM K₂Cr₂O₄ solution (pH ~5). Then this slurry was illuminated for 3 hours under UV light (3.2 mW/cm²). After photodeposition, the powder was filtered and dried at 80 °C for 12 hours. The amount of Cr₂O₃ deposited was verified to be 0.2 wt%.

4.2.2 Sample characterization

XRD measurements were performed on a Bruker D2 (Cu α source) diffractometer. Raman spectroscopy was performed at room temperature using a Raman spectrometer (Avantes AvaRaman) equipped with a 785 nm laser. A Philips PW 1480 analyzer was used for XRF analysis. TEM imaging of the fresh and measured Cr₂O₃-modified Ni/NiO-Mg:SrTiO₃ was performed using a JEOL 2010-F microscope equipped with an EDAX detector.

4.2.3 ICP measurement

ICP-OES: The Cr, Mg, and Ni concentrations in the solution at different stage of the photocatalytic water splitting procedure were determined by Inductively coupled plasma optical emission spectroscopy (ICP-OES), using a Perkin Elmer 8300dv instrument. In short, the catalyst powder (Mg:SrTiO₃-NiO_x composite or Mg:SrTiO₃-NiO_x-Cr₂O₃ composite) was isolated from the slurry solution at different stage, then the isolated clear solution is measured by ICP-OES. Reaction condition: 25 mg catalyst in 25 mL DI water.

ICP-MS: The in situ ICP-MS measurements were conducted in a scanning flow cell (SFC) connected to an inductively coupled plasma mass spectrometer (ICP-MS) (NexION 300X, Perkin Elmer). The catalyst samples (SrTiO₃-NiO_x, Mg:SrTiO₃-NiO_x, Mg:SrTiO₃-NiO_x-Cr₂O₃) were drop casted on a glassy carbon substrate. Each spot was loaded with 15 µg catalyst with a spot size of around 1.2 mm. The schematic working procedure is shown in figure 4.11 and each measurement required 30 min.

4.2.4 Photocatalytic activity experiments

The photocatalytic activity of the compounds was measured using a continuously stirred tank reactor connected to a highly sensitive gas chromatograph (CompactGC Interscience). The GC was equipped with a Pulsed Discharge Detector. By a constant helium (7N) purge (10 mL/min), the gas to be analyzed was transferred to the GC. The optical glass reactor (402.013-OG, Hellma) was illuminated by a 1.5 AM solar simulator (ABET technologies model 10500 low cost solar simulator, 4.9 cm² beam area), which is representative of the intensity profile of solar radiation. The apparent quantum efficiency was measured using 365 nm LED illumination (Roithner LaserTechnik), with a measured intensity of 1.9 mW/cm² and an area of illumination of 2.25 cm².

4.3 Results and discussions

4.3.1 Characterization

Figure 4.1. XRD patterns of pristine Mg:SrTiO₃, Mg:SrTiO₃-NiO_x composite, and Mg:SrTiO₃-NiO_x-Cr₂O₃ composite.

Structural characterization of different material compositions by XRD is shown in figure 4.1. The X-ray diffraction patterns of Mg:SrTiO₃ are consistent with the typical SrTiO₃ cubic structure. After depositing NiO_x and Cr₂O₃ on the surface, the cubic phase remains, illustrating that incorporation of NiO_x or Cr₂O₃ in the lattice is minimized. The Raman spectra of various composites are shown in figure A4.1 (see appendix). Two typical SrTiO₃ bands center in the 200-400 cm⁻¹ and 600-800 cm⁻¹ ranges¹⁷, indicative of SrTiO₃, while features of NiO_x and Cr₂O₃ remain undetected.

The morphological features of the composites are compared in Figure 4.2. The freshly prepared Ni/NiO-Mg:SrTiO₃ composite, and the Cr₂O₃ promoted composite, show a high degree of crystallinity. NiO_x nanoparticles are evenly distributed on the surface of the materials, with particle sizes around 10 nm. The

deposition of Cr_2O_3 does not significantly alter particle sizes (figure 4.2 d), and novel, potentially Cr_2O_3 or mixed metal oxide particles, are difficult to identify.

Figure 4.2. HRTEM images of fresh $\text{Mg}:\text{SrTiO}_3\text{-NiO}_x$ composite (a, b) and fresh $\text{Mg}:\text{SrTiO}_3\text{-NiO}_x\text{-Cr}_2\text{O}_3$ composite (c, d).

In addition, the surface distribution of NiO_x and Cr_2O_3 was verified by TEM-EDX. Figure 4.3 displays the EDX spectra which are collected for the bulk and surface of the particles. As indicated, Mg is consistently present throughout the bulk and surface, indicating Mg is incorporated into the structure of SrTiO_3 . In contrast, the Cr, Ni, and O signals clearly increase near the surface, which corroborates the surface deposition of NiO_x and Cr_2O_3 .

Figure 4.3. TEM-EDX spectra of the fresh Mg:SrTiO₃-NiO_x-Cr₂O₃ composite: Black line for bulk and green line for surface.

The oxidation states of NiO_x co-catalyst on the surface of NiO_x-Mg:SrTiO₃ and Cr₂O₃-modified NiO_x-Mg:SrTiO₃ were verified by XPS for both, as-prepared, and measured samples. The obtained Ni2p_{3/2} signals are shown in Figure 4.4 and O1s signals are shown in figure A4.3 (see appendix). Similar to what was observed in chapter 2, deconvolution (not shown) of the Ni 2p_{3/2} signal confirms the presence of metallic Ni⁰ (851.9 eV) and Ni²⁺ (NiO at 853.5 eV) in freshly prepared NiO_x-Mg:SrTiO₃ (Figure 4.4(a)). After illumination, the width and the symmetry of the Ni signal have changed, which suggests the relative contribution of Ni²⁺ (as in Ni(OH)₂ at 855.6 eV) is significantly enhanced as compared to Ni⁰. As suggested in chapter 2, formation of NiOOH might also contribute to the spectral observations. The changes in the O1s signal (figure A4.3, see appendix) induced by illumination, confirm the changes in Ni oxidation state. In contrast, the Ni signals and O signals of the Cr₂O₃-modified NiO_x-Mg:SrTiO₃ composite show little difference, before and after illumination (Figure 4.4(b)), suggesting that NiO_x preserves the same oxidation state (Ni²⁺ (as in Ni(OH)₂ at 855.6 eV) and presumably some NiOOH). The dominant presence of oxidized Ni-species in the as- prepared Cr₂O₃-modified NiO_x-Mg:SrTiO₃ is likely due to the applied photodeposition procedure, in which the oxidation of Ni from low to higher oxidation has apparently occurred.

Figure 4.4. XPS spectra of the $\text{Ni}2p_{3/2}$ signal of $\text{Mg}:\text{SrTiO}_3\text{-NiO}_x$ composite (a) and $\text{Mg}:\text{SrTiO}_3\text{-NiO}_x\text{-Cr}_2\text{O}_3$ composite (b): (both fresh and measured samples).

4.3.2 Photocatalytic experiment

Figure 4.5. Photocatalytic water splitting behavior of $(\text{Cr}_2\text{O}_3\text{-modified}) \text{NiO}_x\text{-Mg}:\text{SrTiO}_3$ composite using 365 nm LED light illumination. Reaction condition: 25 mg catalyst in 25 mL DI water.

Photocatalytic water splitting experiments are shown in Figure 4.5. Similar to our previous results (in chapter 3), a typical transient in gas production appears for NiO_x-Mg:SrTiO₃ when illumination is initiated, which is due to structural changes and changes in oxidation state of core/shell Ni/NiO particles¹¹. The NiO_x-Mg:SrTiO₃ composite also shows a typical deactivation transient in gas production, while the application of Cr₂O₃ significantly improves the activity and stability. Extending the illumination time to 70 hours, Cr₂O₃-promoted Ni/NiO-Mg:SrTiO₃ preserved 90% of the initial photocatalytic activity after 70 hours of operation, see Figure A4.4 (Appendix). Considering the photon flux of 365 nm LED light, the apparent quantum efficiencies are calculated to be 15% and 30% for Ni/NiO-Mg:SrTiO₃ and Cr₂O₃-promoted Ni/NiO-Mg:SrTiO₃, respectively. Moreover, the photocatalytic activity using 365 nm LED light is ~2 times higher than using solar-light illumination (not shown), highlighting the relatively high absorption cross-section of SrTiO₃ at 365 nm, as compared to wavelengths in the range of 365-400 nm. In the following paragraphs we discuss two possible explanations for the positive effect of Cr₂O₃, being protection of Ni against H₂ oxidation, or formation of mixed metal oxides, inhibiting leaching and reconstruction of constituents (Mg, Ni) of the active composite.

4.3.3 Investigation of O₂ reduction

It has been reported that Cr₂O₃ suppresses electrochemical ORR during photocatalytic water splitting reactions⁹, as well as in the dark ($\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$), especially in batch type reactors. To verify Cr₂O₃ protects Ni against these reactions, two approaches were used.

Firstly, a mixture of H₂, O₂ and N₂ (all in concentration of 80 ppm) in helium was used as purging gas, instead of pure He. Figure 4.6 shows the photocatalytic performance of (Cr₂O₃ promoted) NiO_x-Mg:SrTiO₃. In the absence of light, the measured concentrations in the reactor effluent are equal to the feed concentrations at around 80 ppm, showing that neither catalyst formulation induces thermal reduction of O₂. Once initiating illumination, H₂ and O₂ are produced in similar amounts as shown in Figure 4.5. NiO_x-Mg:SrTiO₃ again shows deactivation and Cr₂O₃ promoted NiO_x-Mg:SrTiO₃

shows significantly more stable gas production. Terminating illumination results in a fast transient in gas production, quickly stabilizing at the background levels. Re-initiating illumination recovers gas production, with $\text{NiO}_x\text{-Mg:SrTiO}_3$ continuing deactivation. Using values after 450 minutes of illumination, and correcting concentrations for feed composition, an apparent quantum efficiency of 15% or 30% can be calculated for each catalyst system, showing (prevention) of light induced reduction of oxygen does not explain the positive effect of addition of Cr_2O_3 to $\text{NiO}_x\text{-Mg:SrTiO}_3$. Figure A4.8 (see appendix) further confirms this conclusion, showing the result of introducing 80 ppm of H_2 , O_2 and N_2 during the experiment. The gas evolution rate is hardly influenced by introduction of the gas mixture.

Figure 4.6. Photocatalytic activity of $\text{Mg:SrTiO}_3\text{-NiO}_x$ (a) and $\text{Mg:SrTiO}_3\text{-NiO}_x\text{-Cr}_2\text{O}_3$ (b) composite with a purge of a mixture of standard H_2 , O_2 and N_2 (all at 80 ppm). Reaction condition: 25 mg catalyst in 25 mL DI water with 365 nm LED as the light source.

Secondly, the partial pressure of produced H_2 and O_2 can be influenced by the flow rate of He introduced in the CSTR reactor. The rate of reduction of oxygen is likely pressure-dependent, thus varying the flow rate should affect the rate of reduction of O_2 , when present¹⁸. The effect of flow rate on the performance of $\text{NiO}_x\text{-Mg:SrTiO}_3$ and Cr_2O_3 promoted $\text{NiO}_x\text{-Mg:SrTiO}_3$ is shown in figure 4.6. For both catalyst formulations, changing the flow rate from 10 mL/min to 5 mL/min results in a twofold increase in product-gas concentration (H_2 from 160 ppm to 320 ppm and 200 ppm to 400 ppm, respectively). Changing the flow rate to 5 mL/min result in the equivalent threefold decrease in gas concentrations. Since the produced gas concentrations are hardly influenced by the flow rate of

the purge-gas, similar production rates can be calculated, as shown in Figure A4.6 and A4.7 (see appendix). Summarizing, Ni appears a poor catalyst for reduction of oxygen at the concentrations relevant for the present study, and protection of Ni by Cr₂O₃ is thus unlikely to explain the enhanced performance of Cr₂O₃ promoted NiO_x-Mg:SrTiO₃.

Figure 4.7. Photocatalytic activity of Mg:SrTiO₃-NiO_x (a) and Mg:SrTiO₃-NiO_x-Cr₂O₃ (b) with changing the purging helium flow rate. Reaction condition: 25 mg catalyst in 25 mL DI water with 365 nm LED as the light source.

4.3.4 Formation of mixed metal oxides

To assess formation of Mg-containing mixed metal oxides, the steady state performance of NiO_x-Mg:SrTiO₃ was compared to NiO_x-SrTiO₃, before and after deposition of Cr₂O₃ (Figure 4.8). Both pristine Ni/NiO-SrTiO₃ and Ni/NiO-Mg:SrTiO₃ composites show significant steady state hydrogen evolution rates, while Mg incorporation significantly enhances the photocatalytic activity, as previously reported (chapter 3). Deposition of Cr₂O₃ enhances the photocatalytic performance of NiO_x-Mg:SrTiO₃ (from 2.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ to 5.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) more significantly than of NiO_x-SrTiO₃ (the H₂ production rate increases from 0.8 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ to 0.9 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$). Furthermore, in the absence of Mg, Cr₂O₃ does not entirely prevent the decreasing transient in evolution rate of H₂ and O₂ (see appendix figure A4.5). These observations suggest formation of a mixed metal oxide of MgO and CrO_x might be relevant for the increased activity and stability of NiO_x-SrTiO₃.

Figure 4.8. Photocatalytic steady state rate of NiO_x-SrTiO₃ and NiO_x-Mg:SrTiO₃ in the absence or presence of Cr₂O₃. Reaction condition: 25 mg catalyst in 25 mL DI water with 365 nm LED as the light source.

4.3.5 Leaching of elements from the composite

4.3.5.1 ICP-OES measurements based on the catalyst solution

Although we have explained the initial transient in hydrogen and oxygen evolution rates of NiO_x-SrTiO₃ composites by changes in physical appearance and oxidation state of Ni-species (chapter 2), the slow continuous deactivation of the NiO_x-SrTiO₃ and NiO_x-Mg:SrTiO₃ composites has not been previously addressed. Leaching of Ni into solution might be responsible for this observation. ICP-OES was applied to determine similarities or differences in leaching behavior of Ni, (and Mg), before and after deposition of Cr₂O₃. Analysis of the solution was performed in various stages of a photocatalytic water splitting experiment, as shown in Figure 4.9.

Figure 4.9. Schematic illustration of the stages of a photocatalytic water splitting experiment in which solution was extracted and analyzed by ICP-OES. Reaction condition: 25 mg catalyst in 25 mL DI water.

As indicated in Figure 4.10, some Ni (Figure 4.10a), and significant amount of Mg have dissolved into the solution upon deposition of Cr_2O_3 from the $\text{K}_2\text{Cr}_2\text{O}_4$ solution. Focusing on the Ni-content in solution, Figure 4.10a shows that the $\text{NiO}_x\text{-SrTiO}_3$ composite continuously leaches Ni once immersed into water (red bars), up to a value of 0.35 mg/L after illumination. Surprisingly, the $\text{NiO}_x\text{-Mg:SrTiO}_3$ composite exhibits a maximum in leached amount of Ni after purging the solution for 3 hours (0.28 mg/L), after which Ni appears to redeposit on the composite (blue bars). For the Cr_2O_3 -modified samples, leaching is less significant and constant in quantity after 3 hours of purging of the solution (brown bars), and even smaller in quantity for the Mg-containing composite (yellow bars). Focusing on Mg, the presence of NiO_x appears to suppress leaching (compare green and blue bars in Figure 4.10b). Addition of Cr_2O_3 further suppresses Mg-leaching, which is most significant after illumination (after measurement). Assuming leaching is negatively affected (less significant) by formation of mixed metal-oxides, the results suggest Ni and Mg are constituents of such mixed metal-oxide, which appears variable in composition as a function of the time of exposure to the aqueous solution (re-

deposition of NiO_x , and continuous leaching of Mg(O)). Following the reasoning that reduced leaching is due to formation of mixed-metal oxides, the stable, and effective catalyst particles appear to consist of a mixed CrMgNiO_x . Further characterization of such particles is necessary and ongoing to confirm the presence of such species.

Figure 4.10. ICP-OES results of Ni and Mg contents in the solution: (a) Ni content; (b) Mg content. Catalyst concentration: 25 mg in 25 mL DI water for all the measurements.

4.3.5.2 In situ ICP-MS measurements

In situ ICP-MS was applied to determine kinetics of Ni, Mg, and Cr dissolution, also including determination of Sr. Continuous liquid flow experiments were performed as illustrated in Figure 4.11 and 4.13

Figure 4.11. Illustration of the applied ICP-MS measurement.

For this ICP-MS measurement, 15 µg of each catalyst was drop-casted on a glassy carbon substrate with the spot-size being around 1.2 mm. The results of ICP-MS measurements on catalyst samples (SrTiO₃-NiO_x, Mg:SrTiO₃-NiO_x, and Mg:SrTiO₃-NiO_x-Cr₂O₃) are shown in figure 4.12.

Figure 4.12. a) ICP-MS results of accumulated liquid content with a measurement time of 30 minutes consisting of an initial 10 minutes of aqueous flow in darkness, illumination for 10 minutes, and additional aqueous flow for 10 minutes in darkness. b) accumulation by the 10 minutes of illumination. Measurement condition: 15 µg per catalyst and 186 µL/min of water flow.

As shown in figure 4.12, Sr leaches rapidly from all three samples to large accumulated quantities within 30 mins of flow, and most significantly in the presence of Mg. Following an initial flush time of 10 minutes, the amount accumulated in (an additional) 10 minutes of illumination at 385 nm is small (Figure 4.12b). It should be mentioned that initiating and terminating illumination did not result in significant transients in leaching rate of Sr. Figure 4.14 further illustrates leaching behavior of Ni. Leaching is rapid and predominant in the first 10 minutes of aqueous flow. Similar to Sr, it should be mentioned that initiating and terminating illumination did not result in significant transients in leaching rate Ni. Leaching of Ni is suppressed by the presence of Mg, in agreement with the comparison presented in Figure 4.10a after prolonged purging of the solution (for 12 h). The addition of Cr₂O₃ appears to further enhance the Ni stability, although it should be mentioned that the initial Ni-content of the sample might be lower as the result of dissolution of Ni in the K₂Cr₂O₄ solution used for Cr₂O₃ deposition.

Figure 4.13. Schematic illustration of the ICP-MS measurement.

Figure 4.14. ICP-MS results of integrated Ni content over 30 mins measurements. Measurement condition: 15 μ g per catalyst under 186 μ L/min of water flow.

The ICP-MS results are largely in agreement with the ICP-OES results, showing that leaching is likely reduced due to formation of mixed-metal oxides. How leaching of Sr affects catalytic activity, remains topic of future studies.

4.4 Conclusion

Deactivation of the NiO_x-Mg:SrTiO₃ catalyst is frequently observed, and likely due to demonstrated leaching of Ni and/or Mg. Deposition of Cr₂O₃ significantly enhances activity and stability. The positive effect is not related to suppression of the oxidation of H₂, by formation of e.g. a core-shell Ni@Cr₂O₃ structure, but rather due to formation of a mixed metal oxide phase, presumably consisting of NiMgCrO_x, which induces reduced susceptibility to leaching of Ni and Mg. Under optimal conditions, a quantum efficiency of 30% is obtained. Even though the Cr₂O₃ protects Mg and Ni leaching, the mechanism behind this is still not clear. Also, how the interaction between Cr and Mg/Ni during POWS and how the Sr leaching influences the photocatalytic activity still need to be further verified.

4.5 References

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4.6 Appendix

Figure A4.1. Raman spectra of $\text{NiO}_x\text{-Mg:SrTiO}_3$ and Cr_2O_3 promoted $\text{NiO}_x\text{-Mg:SrTiO}_3$.

Figure A4.2. Diffuse-reflection spectra (in Kubelka-munka units) of Mg:SrTiO_3 and SrTiO_3 .

Figure A4.3. XPS spectra in the O1s region of both fresh and measured samples of $\text{NiO}_x-\text{Mg}:\text{SrTiO}_3$ (a) and Cr_2O_3 -promoted $\text{NiO}_x-\text{Mg}:\text{SrTiO}_3$ composite (b).

Figure A4.4. Measurement of photocatalytic stability of Cr_2O_3 -promoted $\text{NiO}_x-\text{Mg}:\text{SrTiO}_3$. Reaction conditions: 25 mg catalyst in 25 mL DI water and 365 nm LED-light was used as illumination source.

Figure A4.5. Photocatalytic performance of $\text{NiO}_x\text{-SrTiO}_3$ and Cr_2O_3 -promoted $\text{NiO}_x\text{-SrTiO}_3$. Reaction conditions: 25 mg catalyst in 25 mL DI water and 365 nm LED-light was used as illumination source.

Figure A4.6. Photocatalytic activity of $\text{NiO}_x\text{-Mg:SrTiO}_3$ at variable purge gas rates. (a) the measured concentration of H_2 and O_2 in ppm, (b) the corresponding rate. Reaction conditions: 25 mg catalyst in 25 mL DI water and 365 nm LED-light was used as illumination source.

Figure A4.7. Photocatalytic activity of Cr_2O_3 -promoted $\text{NiO}_x\text{-Mg}:\text{SrTiO}_3$ at variable purge gas rates. (a) the measured concentration of H_2 and O_2 in ppm, (b) the corresponding rate. Reaction conditions: 25 mg catalyst in 25 mL DI water and 365 nm LED-light was used as illumination source.

Figure A4.8. Photocatalytic activity of Cr_2O_3 -promoted $\text{NiO}_x\text{-Mg}:\text{SrTiO}_3$ with introduction of 80 ppm of H_2 , O_2 and N_2 between 150 minutes and 300 minutes. Reaction conditions: 25 mg catalyst in 25 mL DI water, 365 nm LED-light was used as illumination source.

Chapter 5

A comparative analysis of Mg- and Al-modified SrTiO_3 in photocatalytic water splitting

Various heterogeneous photocatalysts are active for overall water splitting. Just recently, high apparent quantum efficiencies (AQE) were reported for Mg- and Al -modified SrTiO_3 photocatalysts ($\text{Al}:\text{SrTiO}_3$ and $\text{Mg}:\text{SrTiO}_3$). In this study, we systematically evaluate the behavior of these catalysts, functionalized with a $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ co-catalyst, focusing on optimized catalyst concentration, behavior in transient operation (on-off cycles to mimic day-night cycles), and long term stability. $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ functionalized $\text{Al}:\text{SrTiO}_3$ and $\text{Mg}:\text{SrTiO}_3$ provide optimized behavior of a CSTR at similar catalyst concentrations of 1 g/L, both providing an apparent quantum efficiency (AQE) of ~32% at 360 nm. However, $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ functionalized $\text{Al}:\text{SrTiO}_3$ shows faster transient to steady state operation after initiation of illumination, and better long term stability. Based on the results of chapter 4, we discuss the slower transient and inferior stability of $\text{Mg}:\text{SrTiO}_3$ on the basis of restructuring of $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ induced by leaching of Mg and Sr. Interestingly, when the solution (water) is refreshed, $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ functionalized $\text{Mg}:\text{SrTiO}_3$ regains activity, which is similar to the as-prepared formulation. Still, $\text{Al}:\text{SrTiO}_3$ appears the preferred catalyst for practical application.

5.1 Introduction

Storing solar light to in chemical bonds is considered a feasible method to contribute to the energy transition from fossil to renewable sources.^{1–3} To this end, semiconductor-based photocatalytic water splitting needs to be developed.^{4,5} To date, various promising photocatalysts have been reported.^{6–9} In particular, semiconductor oxides with d^0 and d^{10} electronic state have been shown to drive photocatalytic overall water splitting.^{10,11} For instance, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ loaded with RuO_2 co-catalysts was reported to yield stoichiometric H_2 and O_2 production under visible light illumination.¹² Replacing RuO_2 by $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ co-catalyst resulted in an increase in quantum yield (QY) from 0.14% to 2.5%.¹³ Most recently, doping of SrTiO_3 with lower valence cations^{14–17}, such as Na^+ , Rh^{3+} , Al^{3+} and Mg^{2+} , has been shown to significantly enhance photocatalytic overall water splitting activity of SrTiO_3 . Using $\text{Al}:\text{SrTiO}_3$, functionalized with a $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ co-catalyst, an apparent quantum efficiency (AQE) of 30% at 360 nm was achieved. In our recent work, we reported a similar AQE for photocatalytic water splitting using $\text{Mg}:\text{SrTiO}_3$, functionalized with a $\text{Ni}_x\text{Cr}_y\text{O}_z$ co-catalyst. Although the presence of Cr_2O_3 stabilized the active Ni-phase, leaching of Ni could not be completely prevented (see chapter 4).

This study reports on the evaluation of the $\text{Al}:\text{SrTiO}_3$ and $\text{Mg}:\text{SrTiO}_3$ semiconductors equipped with the same $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ co-catalyst in overall water splitting. We followed the comparative approach reported by Takanabe and co-workers,¹⁸ using consistent reaction conditions, such as (transients in) spectral irradiance, temperature, and the applied continuously stirred tank reactor (CSTR). We particularly compared performance at different catalyst concentration. In addition, we focused on transient behavior in on-off cycles to mimic day-night cycles, and we report long term stability of both catalysts. While the previously reported similar AQE of 30% for both semiconductors is confirmed, differences in transient operation (day-night cycles) were observed, as well as differences in long term stability. These differences will be tentatively explained on the basis of leaching of several components of the $\text{Mg}:\text{SrTiO}_3$ formulation.

5.2 Experimental section

5.2.1 Material preparation

Mg-modified SrTiO₃. Typically, two steps were applied in the procedure. First, MgSO₄ was mixed with Rutile (TiO₂) and treated at 800 °C, followed by mixing with SrCO₃ and calcination at 1100 °C for 10 hours. The details of the procedure are described chapter 3, and only pure phase Sr_{1.25}Mg_{0.3}TiO_x was used in this study, named as Mg:SrTiO₃.

Al-modified SrTiO₃. Al:SrTiO₃ loaded with Rh_{2-y}Cr_yO₃ co-catalyst was received, and used as prepared by the research group of Frank E. Osterloh, UC at Davis. The details of the procedure have been recently reported.²⁶

Rh_{2-y}Cr_yO₃ co-catalyst loading. The Rh_{2-y}Cr_yO₃ co-catalyst was deposited on both Al:SrTiO₃ and Mg:SrTiO₃ by a previously reported impregnation method.¹⁹ Briefly, 0.1g of Al:SrTiO₃ or Mg:SrTiO₃ powder was dispersed in a solution of 9.6×10⁻⁴ mmol Na₃RhCl₆ and 2×10⁻³ mmol Cr(NO₃)₃·9H₂O. The obtained mixture was stirred for 2 h and the solution evaporated till dryness at 80 °C overnight. The obtained powder was annealed at 350 °C for 1 h in flowing air (30 mL/min) in a tube furnace. The targeted loading was 0.1 wt% Rh and 0.1 wt% Cr (metal content), which was previously reported to yield optimized performance for Al:SrTiO₃.²⁶

5.2.2 Sample characterization

XRD measurements were performed on a Bruker D2 (Cu K α source) diffractometer. Raman spectroscopy was performed at room temperature using a Raman spectroscopy (Bruker Senterra) was performed at room temperature with a 532 nm green laser (2 mW). A Nova 600-nanolab HR-SEM (FEI instruments) was used for SEM experiments. Samples for TEM analysis were prepared by dispersion in ethanol, and deposition onto a carbon coated TEM grid. UV-Vis diffuse reflectance spectra (DRS) were recorded with a UV-Vis spectrophotometer (Thermo Scientific, Evolution 600), the reflectance data were converted to Kubelka-Munk plots.

5.2.3 Light intensity measurement

A 365 nm LED light-source (Roithner LaserTechnik) with a measured intensity of 1.9 mW/cm^2 was positioned in front of a standard quartz UV/vis cuvette ($1 \times 1 \text{ cm}$). Behind the cuvette, a UV/Vis probe was positioned, connected to an Avantes AvaSpec-ULS2048XL-EVO spectrometer. The position of the probe could be varied, to determine the position of optimized intensity. Aqueous solutions containing various catalyst concentrations of $\text{Al}:\text{SrTiO}_3$ and $\text{Mg}:\text{SrTiO}_3$ were prepared and continuously stirred in a beaker using a magnetic stirrer. Each of these catalyst concentrations were injected in the cuvette using a pipette, and the light attenuation was measured within one minute of introduction of the catalyst solution, to minimize sedimentation of the solid.

5.2.4 Photocatalytic activity experiments

The photocatalytic activity of the compounds was measured using a continuously stirred tank reactor. The optical glass reactor (402.013-OG, Hellma) was illuminated by a solar simulator (ABET technologies model 10500 low cost solar simulator, 4.9 cm^2 beam area), which is representative of the intensity profile of solar radiation. The slurry reactor was purged by a constant helium flow (7N, 10 mL/min). The exhaust of the reactor was connected to a highly sensitive gas chromatograph (CompactGC Interscience).²⁰ The GC was equipped with a Pulsed Discharge Detector (PDD), possessing high sensitivity and allowing product detection with 2 minute time-resolution. A Q-bond column was required to remove H_2O from the gas flow, and the products were separated on a Molsieve 5A column.

5.3 Results and discussions

5.3.1 Material Characterization

Figure 5.1. XRD patterns (a) and Raman spectra (b) of pristine SrTiO₃ and nd Al:SrTiO₃ and Mg:SrTiO₃.

XRD characterization of Al:SrTiO₃ and Mg:SrTiO₃ reveals the cubic structure of pristine SrTiO₃.²¹ The FWHMs of the (110) diffraction line are calculated to be 0.431 for SrTiO₃, 0.335 for Al:SrTiO₃ and 0.194 for Mg:SrTiO₃, respectively. The reduced FWHM for the doped SrTiO₃ compositions, indicates that the incorporation of Mg or Al in the lattice enhances the crystallinity of SrTiO₃,¹⁶ which is also reflected by differences in the crystallite size (Table 5.1). The corresponding Raman spectra of the three materials are shown in Figure 5.1b. For the pristine SrTiO₃ the standard second-order scattering pattern with two dominating regions (200-400 cm⁻¹ and 600-800 cm⁻¹) is obtained.²² For Mg:SrTiO₃ the Raman spectrum is also very similar, indicating that the cubic SrTiO₃ crystalline structure is preserved after Mg-modification. In the Raman spectrum of the Al:SrTiO₃ composite, the intensity of the three apparent contributions to the 200-400 cm⁻¹ and 600-800 cm⁻¹ regions appear in different ratio, although the overall appearance of the spectra is similar to SrTiO₃ and Mg:SrTiO₃. This is probably due to a slightly different local crystal symmetry, as a result from the different synthesis methods.

Table 5.1. FWHM of the (110) peak, and the calculated crystallite size based on the Scherrer equation.

Sample	FWHM of (110) peak	Crystallite size
Pristine SrTiO₃	0.431	20.1 nm
Al:SrTiO₃	0.335	25.8 nm
Mg:SrTiO₃	0.194	44.8 nm

Figure 5.2. Kubelka-Munk diffuse reflectance of the unmodified materials.

The optical properties of the pristine semiconductors (in absence of the Rh₂-yCr_yO₃ co-catalysts) are shown in Figure 5.2. Pristine SrTiO₃ allows light absorption in the UV range below 390 nm, which is corresponding to the reported band gap energy of 3.2 eV.²³ After incorporating Al or Mg into the structure of SrTiO₃, a blue shift in band gap energy is observed. Mg-doping increases the band gap to 3.3 eV, while Al:SrTiO₃ shows a band gap of 3.4 eV.²⁶ The enlargement of the band gap is likely due to replacement of either Sr²⁺ or

Ti⁴⁺ by Al³⁺ or Mg²⁺.¹⁵ The discrepancy in the charges of different elements, would create oxygen vacancies in SrTiO₃, resulting in differences in electronic structure.

The morphology of both Al:SrTiO₃ and Mg:SrTiO₃ with the same amount of Rh_{2-y}Cr_yO₃ (0.1wt% Rh + 0.1wt% Cr) on the surface was investigated by HRSEM (figure 5.3). As shown in the SEM images, Al:SrTiO₃ obtained by the flux treatment method consists of several cubic particles, appearing in a broad size-range distribution of 200 nm to 2μm. Mg:SrTiO₃ consists of mostly irregularly shaped, sintered particles, while the size range-distribution of the particles is smaller, ranging from 200 to 400 nm. Due to the low loading of the Rh_{2-y}Cr_yO₃ particles, these cannot be resolved by SEM.

HRTEM is applied to further investigate the appearance of the Rh_{2-y}Cr_yO₃ co-catalyst particles on the surfaces of Al:SrTiO₃ and Mg:SrTiO₃. Figure 5.4 shows the cubic morphology of Al:SrTiO₃, with small, rather individual, nanoparticles present on the surface. The estimated size of the individual particles is in the order of 5 nm, although larger agglomerates can also be observed. The Rh_{2-y}Cr_yO₃ particles on the surface of Mg:SrTiO₃ appear more aggregated, and are more difficult to observe. The aggregates show an average size in the order of 10 nm.

Figure 5.3. HRSEM images of Al/Mg modified SrTiO_3 with the same amount of $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ co-catalyst on the surface (0.1wt% Rh + 0.1wt% Cr). (a, b) $\text{Al:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ (c, d) $\text{Mg:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$.

Figure 5.4. HRTEM images of Al/Mg modified SrTiO_3 with the same amount of $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ co-catalyst on the surface (0.1wt% Rh + 0.1wt% Cr). (a, b, c) $\text{Al:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$, (d, e, f) $\text{Mg:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$.

5.3.2 Photocatalytic activity

The photocatalytic performance of Al:SrTiO₃ and Mg:SrTiO₃, both equipped with Rh_{2-y}Cr_yO₃ (0.1wt% Rh + 0.1wt% Cr), is compared at a catalyst concentration of 1 g/L (figure 5.5).^{16,24,25} The CSTR rapidly reaches steady state performance in the case of Al:SrTiO₃ (Figure 5.5a). The hydrogen evolution rate amounts to 0.11 $\mu\text{mol}\cdot\text{min}^{-1}$, equivalent to an apparent quantum efficiency (AQE) of 32%, in agreement with literature.²⁴ The catalyst shows the expected ratio of H₂ over O₂ of 2:1, and maintains the AQE during prolonged illumination of up to 8 hrs. The hydrogen evolution rate (0.09 $\mu\text{mol}\cdot\text{min}^{-1}$) and apparent quantum efficiency of the Mg:SrTiO₃-Rh_{2-y}Cr_yO₃ composite is lower at 26%, again showing a 2:1 ratio of H₂ over O₂ in steady state conditions. The lower (steady state) performance of Mg:SrTiO₃ is in agreement with a previously reported comparative study on doping of SrTiO₃ with Al³⁺, Mg²⁺ and Ga³⁺. Al doping resulted in a slightly better photocatalytic activity as compared to the other two elements.²⁴ The stability of Mg:SrTiO₃ is also high, but to reach steady state requires a longer period of illumination (Figure 5.5b). This delay in reaching steady-state, as compared to the fast transient observed for Al:SrTiO₃, is hard to explain, but might be related to the initial appearance of the Rh_{2-y}Cr_yO₃ particles (Figure 5.4). These particles show a large degree of clustering and might be redistributed in the initial period of illumination, by e.g. dissolution and re-deposition processes. This requires further investigation.

Figure 5.5. Photocatalytic water splitting transient behavior under solar light illumination: (a) Al:SrTiO₃-Rh_{2-y}Cr_yO₃, (b) Mg:SrTiO₃-Rh_{2-y}Cr_yO₃ (Catalyst concentration: 1 g/L, flow rate: 10 mL/min, solar light illumination).

To further assess the performance of Al:SrTiO₃ and Mg:SrTiO₃, we followed the procedure proposed by Takanabe¹⁸ and his co-workers, and varied the catalyst concentration. Figure 5.6 displays the photocatalytic H₂ production rate plotted as a function of photocatalyst concentration for both photocatalysts, and figure A5.1 and A5.2 (see appendix) show the photocatalytic gas production transients at all different concentrations.

Figure 5.6. Photocatalytic H₂ evolution rate of both Al:SrTiO₃ and Mg:SrTiO₃ with Rh_{2-y}Cr_yO₃ as the co-catalyst under various catalyst concentration.

The H₂ evolution rates are taken from the steady-state plateau after 6 hrs of operation. The optimal (plateau) H₂ evolution rate is reached for Al:SrTiO₃ at a photocatalyst concentration of approx. 1g/L, in agreement with literature. Taking the measurement error into account, steady state H₂ evolution rates of appr. 0.09 ± 0.03 μmol/min are obtained at for Al:SrTiO₃ concentrations > 1g/L, slightly lower than the optimized value (0.11 ± 0.03 μmol/min. at 1g/L). Increasing the catalyst concentration of Mg:SrTiO₃ above 1g/L results in a slightly enhanced H₂ evolution rate of appr. 0.11 ± 0.02 μmol/min, similar to the rate observed for

Al:SrTiO₃ at 1g/L. This limit in photocatalytic efficiency as a function of catalyst concentration for both Al:SrTiO₃ and Mg:SrTiO₃ materials, is due to the exponential nature of light attenuation (as described by the Lambert-Beer Law), limiting the amount of catalyst particles being exposed to light at high concentration. The difference in optimized catalyst concentration might be related differences in optical properties. This will be further evaluated in paragraph 5.3.3.

5.3.3 Light attenuation

The performance of the applied CSTR will depend on the attenuation of light by the catalyst particles in aqueous suspension. As explained in the experimental paragraph, we evaluated the attention of light by Al:SrTiO₃ and Mg:SrTiO₃ using a 365 nm LED light source. Figure 5.7 shows the light attenuation as a function of catalyst concentration. A linear correlation is obtained for both Al:SrTiO₃ and Mg:SrTiO₃. The apparent attenuation coefficient ($\mathcal{E}$) of Mg:SrTiO₃ is larger than that of Al:SrTiO₃, suggesting that Mg:SrTiO₃ attenuates light at 365 nm more efficiently ($\text{g}_{\text{cat}}^{-1}$) than Al:SrTiO₃.

Figure 5.7. light attenuation of Al:SrTiO₃ and Mg:SrTiO₃ at various concentrations.

Even though light is attenuated more effectively by Mg:SrTiO₃ at similar concentrations, the Al:SrTiO₃ catalyst results in better performance of the slurry reactor. This suggests the attenuation coefficient ($\mathcal{E}$) is not only determined by absorption (although absorption is more efficient for Mg:SrTiO₃, in agreement with Figure 5.2), but also by back-scattering of light, outward of the reactor (e.g. towards the light source). This leads to inefficient illumination of particles present in the volume of the reactor. An increasing rate of back-scattering, is typically observed for decreasing agglomerate sizes in suspension. The fraction of back-scattering contributing to the attenuation has been reported to vary between 3.3 to 42% for agglomerates ranging from 2.4 to 0.8 μm in size.²⁷ Although we have not determined the agglomerate size in solution as a function of concentration, the agglomerates of Mg:SrTiO₃ might initially be smaller than of Al:SrTiO₃ at concentrations $< 1\text{g/L}$, while more rapidly increasing in sizes than Mg:SrTiO₃ at higher concentration. In turn this will affect the relative contribution of back-scattering to attenuation for each composite, eventually leading to a different optimized catalyst concentration. Further research is necessary to evaluate the optical properties of the slurry in detail.²⁷

5.3.4 Photocatalytic stability measurements

In order to be practically feasible, the stability of the photocatalytic water splitting system is also an important aspect to be considered. We investigated the photocatalytic stability of the two materials by repeating light-on and light-off experiments, simulating day and night, the results of which are shown in figure 5.8 for Al:SrTiO₃-Rh_{2-y}Cr_yO₃. The stability was evaluated at the respective optimized slurry concentration of 1 g/L. The first three curves were obtained by illumination following an extended period of stirring and purging with He in the dark. Each cycle, the reactor was illuminated for a period of 8 hours. The transient observed in the first graph is fast and in agreement with Figure 5.5a. The second transient shows a slightly different behavior, showing a rapid maximum in rate, followed by a slow decay. The third cycle is very similar, showing further deterioration of the steady state rate. In between the third and the fourth cycle, Al:SrTiO₃-Rh_{2-y}Cr_yO₃ was redispersed in (fresh)

water (followed by continuous purging in the dark) and evaluated for performance.

The steady state rate is somewhat lower than after the third cycle, while the rate appears stable in the fifth, and last cycle. Generally it can be concluded that Al:SrTiO₃-Rh₂-yCr_yO₃ yield fast transients and reaches stable performance after five cycles, at approximately 80% of the initial performance.

Figure 5.8. Photocatalytic stability of Al:SrTiO₃-Rh₂-yCr_yO₃ in pure water solution, and switch light on and off (Catalyst concentration: 1 g/L, flow rate: 10 mL/min).

A similar evaluation of the Mg:SrTiO₃-Rh₂-yCr_yO₃ slurry solution is shown in Figure 5.9 using a catalyst concentration of 2 g/L. The transient observed in the first graph is rather slow and in agreement with Figure 5.5b.

Figure 5.9. Photocatalytic stability of $\text{Mg:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ in pure water solution, and switch light on and off (Catalyst concentration: 2 g/L, flow rate: 10 mL/min).

The two consecutive cycles show a fast and very similar transient to the $\text{Al:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ catalyst, including some deactivation. Interestingly, when this catalyst powder is isolated from the slurry solution, dried, and re-dispersed in fresh water, the shape of the transient resembles the initial experiment, and some steady state activity seems to be regained. The fifth transient is similar to the $\text{Al:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ composite (figure 5.8e), although the steady-state activity is higher. This might be related to the higher initial concentration of 2 g/L, vs 1 g/L for $\text{Al:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$.

To explain the different behavior in day-night cycles, and in particular after re-dispersion, various phenomena can be considered. As demonstrated by the ICP measurements in chapter 4, several elements of $\text{Mg:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ leach into solution, which might affect (re)distribution of the $\text{Rh}_{2-y}\text{Cr}_y\text{O}_3$ catalyst and thus performance. At the same time, the pH of the solution might alter due to instability of the catalyst. As shown in figure 5.10, the pH of the $\text{Mg:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ catalyst solution decreases from 9.8 to 7.6 when maintaining the catalyst powder in water for 24 hours. This pH change might be due to Mg- or Sr-leaching. The pH of the $\text{Al:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ catalyst solution is stable for 30 hours. When isolating the catalyst power out and redispersing into new water solution, the pH of $\text{Mg:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ catalyst solution increases back to 9 again. While, the pH of $\text{Al:SrTiO}_3\text{-Rh}_{2-y}\text{Cr}_y\text{O}_3$ catalyst

solution keeps at 7.6, demonstrating the pH changing is the inducing reason for the transient behavior in the photocatalytic stability measurements.

Figure 5.10. pH measurement of both Al:SrTiO₃-Rh_{2-y}Cr_yO₃ catalyst solution and Mg:SrTiO₃-Rh_{2-y}Cr_yO₃ catalyst solution within 30 hours.

5.4 Conclusion

Al:SrTiO₃ and Mg:SrTiO₃, containing the same Rh_{2-y}Cr_yO₃ catalyst, were compared in overall water splitting. Variation of the catalyst concentration showed similar trends in hydrogen (oxygen) evolution rates, the applied CSTR being most productive at about 1 g/L for Al:SrTiO₃ and 2 g/L for Mg:SrTiO₃. Our experiments show significant differences in transients in the first hour of operation, as-prepared Mg:SrTiO₃ requiring significantly longer time to reach steady state than Al:SrTiO₃. Close to ideal transients were observed after 5 day-night cycles, including refreshing of water in between the third and fourth cycle. Generally both catalyst systems show similar behavior and performance, while initial leaching of Sr and Mg might disfavor practical application of the Mg:SrTiO₃ catalyst formulation.

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5.6 Appendix

Figure A5.1. Photocatalytic efficiency of Al:SrTiO₃- Rh_{2-y}Cr_yO₃ under different catalyst concentration. (a) 0.4 g/L, (b) 0.6 g/L, (c) 1 g/L, (d) 2 g/L, (e) 3 g/L.

Figure A5.2. Photocatalytic efficiency of Mg:SrTiO₃- Rh_{2-y}Cr_yO₃ under different catalyst concentration. (a) 0.4 g/L, (b) 0.6 g/L, (c) 1 g/L, (d) 2 g/L, (e) 3 g/L.

Chapter 6

Driving surface redox reactions in heterogeneous photocatalysis: The active state of illuminated semiconductor supported nanoparticles during overall water splitting

Materials used for photocatalytic overall water splitting (POWS) are typically composed of light-absorbing semiconductor crystals, functionalized with so-called co-catalytic nanoparticles to improve the kinetics of the hydrogen and/or oxygen evolution reactions. While function, quantity, and protection of such metal(oxide) nanoparticles has been addressed in the literature of photocatalysis, the stability and transients in the active oxidation-state upon illumination have received relatively little attention. In this perspective the latest insights in the active state of frequently applied co-catalysts systems, including Pt, Rh/Cr₂O₃ or Ni/NiO_x, will be presented. While the initial morphology and oxidation state of such nanoparticles is a strong function of the applied preparation procedure, significant changes in these properties can occur during water splitting. We discuss these changes in relation to the nature of the cocatalyst/semiconductor interface. We also show how know-how of other disciplines such as heterogeneous catalysis or electro-catalysis, and recent advances in analytical methodology, can help to determine the active state of co-catalytic nanoparticles in photocatalytic applications.

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6.1 Introduction

Photocatalytic conversion of solar energy is considered an ideal route to produce chemical fuels from abundant feed-stocks like water.¹⁻⁴

Photocatalytic overall water splitting (POWS) is a thermo-dynamically unfavourable uphill reaction ($\Delta G > 0$), and to achieve a techno-economically competitive hydrogen production process, it is critical to develop a photocatalytic water splitting system with high solar-to-hydrogen (STH) efficiencies ($> 10\%$) and long-term stability.^{5,6} In photocatalysis, efficiencies are determined by i) the optical proper-ties of the applied semiconductor, i.e. band gap or light absorption efficiency (η_{abs}), and ii) the charge separation efficiency (η_{sep}). Significant progress has been made in the last decades in the development of new semiconductor materials, yet relatively low overall conversion efficiencies of the available (composite) materials have prevented the practical implementation of solar fuel production by (heterogeneous) photocatalysis.⁶

Based on the common perception that optimum performance requires optimized optical and electrical properties; i.e. a bulk band structure that enables absorption of larger fractions of visible light (≤ 600 nm) and efficient separation of generated charge carriers with little loss by recombination, the development of novel semiconductor materials is dominating the research efforts of the community.

In heterogeneous photocatalysis, liquid (aqueous electrolyte)-solid (semiconductor) interfaces are formed. Usually n-type semiconductors are employed, and interfacial charge separation is achieved by an upward band bending caused by the adjustment of the Femi levels of the semi-conductor and the electrolyte (establishing thermodynamic equilibrium).⁷ Upon illumination (using illumination intensities insufficient to establish flat band potentials, e.g. by fully reversing band bending) positive charges generated in the depletion regime will be effectively transferred to the semiconductor/electrolyte interface, whereas electrons are transferred to the bulk. Nevertheless, transfer of the majority carriers (electrons) to the surface is essential to drive the reduction of protons. Therefore, metal nanoparticles are usually employed, which facilitate electron accumulation at the surface (for further information about charge

separation, band bending etc. the readers are referred to existing text books and reviews⁷⁻⁹).

Another important function of the metal(oxide) nanoparticles is to achieve effective POWS by promoting surface reactions (η_{cat})^{10,11}, and in fact a proper alignment of bulk properties and surface catalysis is required to fully utilize the intrinsic properties of a semiconductor for overall water splitting (Figure 6.1). Usually η_{cat} of semiconductor surfaces is low (high overpotentials and slow kinetics for the catalytic H₂ and O₂ evolution or CO₂ reduction) causing severe surface recombination of charge carriers. It is important to emphasize that in comparison to heterogeneous catalysis, in photocatalysis the co-catalytic nanoparticles are not thermally activated, but rather by the light-driven generation of charges in the semiconductor, followed by charge transfer across the interface of the applied semiconductor and the metal(oxide) nanoparticles. After successful transfer of charges (electrons to drive HER) the co-catalysts (electrocatalyst) allow redox reactions by lowering the over-potential of electron transfer reactions, similar to electrocatalysis.^{8,9,12}

Suitable materials for a specific reaction can thus be chosen following the guidelines established by electrochemists.

Figure 6.1. left: Schematic representation of photocatalysis. Illumination of a semiconductor with the efficiency η_{ads} , is followed by charge carrier separation η_{sep} and the surface redox reaction occurring at the surface of the co-catalysts particles η_{cat} . Here, dual co-catalyst functionalization, e.g. hydrogen and oxygen evolution are driven by different co-catalysts. right: Co-catalysts can be dynamic in nature, here a few examples of feasible changes of the co-catalyst are sketched.

For instance, noble and non-noble metals (Pt, Rh, Ru, Au, or Ni)^{13–16}, metal sulfides (e.g. MoS₂ or NiS)^{17,18}, or metal phosphides (e.g. NiP or FeP)¹⁹ are well-known constituents of electrodes used in water or carbon dioxide reduction. The community studying electrochemistry is also well aware of the fact that metal oxides (IrO_x, MnO_x, and CoO_x)^{20–22} and metal oxyhydroxides (NiOOH, or FeOOH)^{23,24} promote water oxidation. Several of these materials (Rh, Ni, Pt for reductive hydrogen evolution) are commonly applied as co-catalysts in heterogeneous photocatalysis. It should be mentioned that in photocatalytic overall water splitting, activity is the primary criterion for selection of the composition of the co-catalytic nanoparticles, while electrochemical selectivity receives little attention.²⁵ An exception is the consideration of the back reaction in water splitting, i.e. the recombination of hydrogen and oxygen to water, since these products are formed in close proximity. Conversion of oxygen and hydrogen to form water can be triggered, i) electrochemically by reduction of oxygen (the Oxygen Reduction Reaction (ORR)) or the oxidation of hydrogen (the Hydrogen Oxidation Reaction, (HOR)) on the hydrogen and oxygen evolution sites of the co-catalysts, or ii) thermally by catalytic activation of hydrogen or oxygen.⁶ While electrochemically induced hydrogen or oxygen activation is only feasible under illumination (initiating the required electrochemistry), thermal activation is feasible in the dark, albeit this is likely enhanced during illumination by the possible presence of local hotspots.

To achieve electrochemical selectivity for the “forward” hydrogen and oxygen evolution from water, in earlier studies solution additives (carbonate salts)²⁶ and sodium hydroxide coatings²⁷ were suggested, whereas in recent literature primarily core-shell structures are used.^{6,25} Frequently applied core-shell structures are chromium oxide (e.g. Rh/Cr₂O₃) or nickel oxide (Ni/NiO_x).⁶ Titanium dioxide and lanthanide oxides were also reported as applicable shell material.²⁸ Here, it is interesting to note that the same principles have already been applied for decades in the chlorate industry showcasing the successful adaption in heterogeneous photocatalysis. In the chlorate industry deposition of a CrO_x film on the cathode is essential to facilitate selective hydrogen formation and to prevent reduction of oxychlorides. Despite its frequent use, the exact

structure, working mechanism, and location of the electrocatalytic hydrogen evolution reaction are not yet exactly known, and consequently the purpose of these oxides in heterogeneous photocatalysis might also be diverse.^{29,30}

Figure 6.2. Relationship between the amount of a co-catalyst and the photocatalytic activity of heterogeneous photocatalyst. Reproduced from ref ³¹. Copyright 2014 Royal Society of Chemistry.

Apart from the benefits of lower overpotentials and favourable kinetics, functionalization of semiconductor surfaces by metallic, metal oxide or even core-shell structured co-catalysts adds additional complexity to the development and understanding of photocatalytic materials.⁶ Different time scales of photoexcitation and catalytic events are still inevitable and positive or negative charging of co-catalysts particles by trapping of charge carriers (in turn potentially increasing η_{sep}) will occur during prolonged illumination.¹¹ Furthermore, the location of the respective co-catalysts driving reductive (H_2 evolution, CO_2 reduction) or oxidative (O_2 evolution) reactions and the interface between the semiconductor surface and the co-catalyst are of importance. The interface has to be carefully designed to generate drift currents by an effective and adequate potential gradient as recently pointed out by Takanabe et al.¹¹ and it is important to realize that these gradients might not be achieved by random arrangement of co-catalyst particles of various sizes.

In contrast to photoelectrocatalytic processes, where materials for reductive and oxidative processes can be optimized independently, for particulate

semiconductor materials favourable interfaces and depositing co-catalysts at preferred locations must be realized on a (single) semiconductor particle, underlining the fact that photocatalysis must be considered as a multidisciplinary field of research. Among others, expertise in semiconductor physics, (in)organic materials chemistry, and (electro-)catalysis is required to develop efficient systems and fully understand individual functions of multicomponent photocatalysts.^{32–34}

The co-catalyst loading is commonly of primary concern and a typical relationship between loading and photocatalysts activity is depicted in Figure 6.2. This simple relationship does not account for differences in the active state of a co-catalyst as a function of loading, nor for the effectiveness of semiconductor/co-catalysts interfaces (potential shifts) and likely overestimates the required co-catalysts loading. Another common mistake is that the same co-catalyst loading (and co-catalyst material) is applied to measure the activity of different semiconductor materials (or the same semiconductor material with for example different morphology). However, optimization of loading and accompanied dispersion of nanoparticles, might be dependent on the applied semiconductor. Moreover, the semiconductor/co-catalyst interface might be different, and these factors determining photocatalytic properties are typically not addressed.³⁵

Heterogeneous photocatalysts are usually tested in recirculating batch reactor systems and their activity is defined by the amount of accumulated gas species detected by methods such as gas chromatography. Due to detection limits and the generally slow data acquisition first data points are only obtained after prolonged illumination of about 1 hour. This realistic and potentially scalable approach (batch-type bags^{5,36}) circumvents that changes in the photocatalytic properties during the “start-up phase” can be revealed. Changes during start-up are known from heterogeneous catalysis, and recently we have shown that dramatic changes in the photocatalytic performance of heterogeneous photocatalysts occur during initial illumination: steady-state activity is only obtained after several minutes/hours.^{37,38} We were able to assign changes in the photocatalytic behavior to changes of the co-catalyst using differential reactor operation and fast product detection.^{36,39}

Summarizing, it is widely recognized that the use of one or more co-catalyst compositions on the surface of a semiconductor is indispensable to achieve high efficiencies.⁴⁰ However, there is still little experimental proof for the operating mechanism and active morphology and oxidation state during photocatalytic operation.^{8,9} Here, we will focus specifically on transients in the composition of co-catalysts upon illumination, and highlight the need to use advanced in-situ, or *operando* characterization methods to determine the "real" active state of co-catalysts. Furthermore, determining dissolved ions after testing and post-catalytic transformations of the co-catalysts, e.g. particle growth, should be revealed. This appears to be especially important for complex core-shell systems. Defining the active state is also mandatory to fully describe the properties of the different interfaces (semiconductor/co-catalyst, semiconductor/electrolyte).

6.2 Transient behavior of Pt and Ni/NiO co-catalysts: Examples of co-catalyst rearrangement

As previously indicated, it is known that a volcano-like shape describes the relationship of co-catalyst loading and photocatalytic activity (Figure 6.2).⁴¹ This simplified dependence ignores transients in composition and deactivation of deposited nanoparticles. The deactivation of a co-catalyst might occur due to:

- i) changes of the light absorbing semiconductor material, e.g. by corrosion;
- ii) changes/rearrangement of the applied co-catalysts, in particular modification of the physio-chemical properties of a co-catalyst, such as oxidation state, phase composition, particle size and atomic structure.

As the stability of photocatalytic composite materials is usually revealed by repetitive testing in batch reactors and subsequent standard (bulk) characterization methods such as X-ray diffraction or UV-Vis spectroscopy, deactivation of the semiconductor can be easily recognized, e.g. for sulfide based materials corrosion is a prominent pathway for deactivation.⁴² These routines might be feasible to predict stability of composite photocatalysts in steady-state conditions, however, deactivation during initial stages of catalytic

testing are not resolved. Furthermore, structural/electronic changes of the co-catalyst present in low quantities on the semiconductor surface are not accessible by standard bulk characterization.

For Pt-modified SrTiO_3 ³⁷, prepared by photodeposition in the absence of sacrificial agents, transients in oxygen evolution were observed and steady-state conditions were only achieved after extended illumination. Surface characterization with particular emphasis on Pt characterization was performed. XPS revealed that the excess of formed oxygen was well-correlated with a reduction of the as-prepared PtO_x to metallic Pt. While the formation of metallic Pt during illumination on an n-type material might not be surprising, these measurements nicely demonstrate that photo-deposition of Pt in the absence of sacrificial agents is a slow process, and full reduction might only be achieved during photocatalytic testing. Moreover, in the same study Pt-modified Rh: SrTiO_3 was prepared and characterized using the same approach. Interestingly, for pre-reduced metallic Pt on Rh: SrTiO_3 oxidation occurred during the testing, and the ‘active’ Pt-species in steady-state conditions resembled PtO_x rather than metallic Pt. Clearly the presence of a dopant not only influences the optical properties of the semiconductor, but also changes the interfacial charge transfer phenomena, and consequently the oxidation state of the co-catalyst (Pt).

In electrochemistry, the oxidation state of active Pt anodes has also been discussed, and generally oxidation of the surface occurs before oxygen is evolved. The chemical potential of the photogenerated holes in the semiconductor are likely sufficient to drive the partial oxidation of Pt to PtO_x in particular on p-type semiconductors. It has been proposed that Rh: SrTiO_3 is in fact a p-type semiconductor.³⁸ Apart from the electrochemically-driven oxide formation, thermal growth of surface oxides must be considered due to the presence of local hot spots governed by intensive illumination. This certainly highlights that post-catalysis-characterization is required to fully describe the composition of a working photocatalyst.

Figure 6.3. A) Gas evolution rates during photocatalytic hydrogen evolution for a series of P25 catalysts loaded with different amounts of Pt. Deactivation is observed at low Pt loadings independent of the pretreatment with ultrasound (US) (e.g., 0.25 wt %), but not at high Pt loadings (≥ 0.75 wt %). Reproduced from ref ⁴³. Copyright 2017 American Chemical Society. B) Time course of hydrogen and oxygen during illumination of a Pt(0.3 wt%)/ TiO_2 photocatalyst in the presence of 0.3 g Na_2CO_3 . The severe changes in evolved H_2 and O_2 clearly point to re-arrangements of the heterogeneous photocatalyst; and C) proposed mechanism of the overall photocatalytic water splitting over Pt- TiO_2 systems in the presence of carbonate salts in aqueous solution. B and C are reproduced from ref ²⁶. Copyright 1997 Royal Society of Chemistry.

Haselmann et al.⁴³ recently reported for Pt-loaded TiO_2 an early stage deactivation after ultrasound pre-treatment. The fast deactivation (within approximately one hour of illumination) was primarily observed for composites with low Pt-loading (Figure 6.3A). The authors related the observed deactivation to a “dynamic” interaction of Pt clusters and/or particles with surface oxygen vacancies. In fact, the authors observed a change in reaction mechanism as well as encapsulation of Pt particles presumably by thin TiO_2 shells. Such strong metal-support interactions (SMSI) are frequently reported in heterogeneous catalysis, however, for heterogeneous photocatalysis the phenomenon is hardly discussed.^{43,44} Finally, it is worth noting that Haselmann et al.⁴³ compared low (= deactivating) and high (= non-deactivating) Pt loading

using similar Pt particle size distributions and Pt leaching or particle migration and growth were excluded as causes of deactivation.

Along these lines, in an earlier study by Arakawa et al.²⁶ the authors report that during illumination of Pt/TiO₂ photocatalysts the Pt was covered with some titanium hydroxide compounds and speculated that the rate of the back reaction was efficiently suppressed. As depicted in Figure 3B the full development of the active photocatalyst required prolonged illumination and therefore it was easily revealed by standard gas chromatography. For the appearance of the SMSI effect-related shell the authors concluded that carbonate addition to the reaction solution is essential. They also concluded that carbonates might be actively involved in the formation of oxygen.

Finally, Li et al.⁴⁵ presented an interesting approach using Pt or PtO_x clusters (approx. 1 nm) loaded on TiO₂ nanosheets to facilitate overall water splitting. Even though some arguments regarding favorable electrochemical selectivity of the PtO_x co-catalyst are questionable, the surface characterization of the materials prior and after photocatalytic experiments are quite interesting and suggest structural rearrangement of the co-catalysts. While the authors argued using prolonged testing, density functional theory, and various characterization techniques that the applied PtO_x co-catalyst is stable, distinct differences in the provided characterization data between as-prepared and tested materials are visible, such as particle growth (by TEM) and (slight) changes in the electronic structure of the PtO_x particles. For the Pt modified TiO₂ sheets, observed changes are more severe and XPS clearly indicates the formation of PtO_x species after catalysis. As indicated above the formation of surface oxides is feasible by electrochemical or thermal oxidation. While the data provided by Li et al.,⁴⁵ did not show transients in gas evolution, the provided characterization data suggest “dynamic” changes of the material during illumination, again highlighting the importance of detailed *post-catalysis* characterization of the co-catalyst.

Figure 6.4. A-B) structure of 1wt % Ni@NiO core/shell particles on TiO₂ after preparation. C) Partial void/shell structures show cleavages in between TiO₂ and Ni metal, and void/shell structures after deactivation of the composite photocatalysts. A-C) Reproduced from ref ⁴⁶. Copyright 2015 American Chemical Society. D) HRTEM images and corresponding FFT results of the (1,2) as-prepared, (3,4) illuminated, and (5,6) regenerated Ni@NiO_x SrTiO₃ composite material. The observed changes in morphology and composition of the Ni@NiO_x co-catalysts during overall water splitting are also schematically indicated. D) Reproduced from ref ³⁸. Copyright 2017 American Chemical Society.

Due to its stability (e.g. Pourbaix diagram⁴⁷) and the well-known performance in HER reaction, Pt is one of the most frequently applied co-catalyst. Another promising candidate is composed of Ni and NiO_x arranged in a core-shell like structure. Core-shell systems are preferred over pure Ni, pure NiO_x and physical mixtures of Ni and NiO_x; in the early work by Domen et al.^{48,49} it was suggested that Ni/NiO_x core-shell particles deposited on SrTiO₃ provide the catalytic sites for hydrogen evolution (Figure 6.4). However, due to the complexity of the co-

catalyst system and the properties of Ni (several feasible oxidation states and feasibility of corrosion), sufficient evidence of the working state of Ni/NiO_x core-shell particles is still missing. Osterloh et al.⁵⁰ suggested that a core-shell model is not representative of the active phase(s). Using surface voltage spectroscopy they demonstrated that the metallic Ni cores function as electron trapping sites and NiO_x shells served as hole trapping sites.⁵⁰ Thus, Ni and NiO_x promote formation of hydrogen and oxygen respectively, making it a dual function co-catalyst. This assignment of functionalities is in agreement with active states known from electrochemical water splitting and leads to an appealing concept in which co-loading of water reduction and oxidation catalyst on the surface of photocatalysts might improve the overall water splitting efficiency.^{6,40}

More recently, we investigated the same system, namely, Ni/NiO_x-modified SrTiO₃ using a differently operated slurry reactor and the fast detection mode of a micro-GC equipped with a Pulsed Discharge Detector (PDD) to investigate the transient performance of H₂ and O₂ evolution in the initial stage of illumination.³⁸ The PDD detector offers significant advantages in sensitivity over conventional TCD detectors, combined with the efficient product separation in μ -GC changes in the product evolution rates on the minute time-scale can be easily achieved. For Ni/NiO- modified SrTiO₃ significant transient in hydrogen evolution accompanied by a sub-stoichiometric H₂:O₂ ratio (> 2), and characterization by XPS and HRTEM suggested that Ni(OH)₂ was oxidized to NiOOH. NiOOH is a well-known OER catalysts, suggesting a promoting effect of oxygen evolution by NiOOH (Figure 6.4). Only after stirring in the dark the required stoichiometric H₂:O₂ ratio was obtained, and ex-situ characterization suggested that severe reorganization of the system occurred, as metallic Ni was embedded in a NiO_x matrix. Finally, Crozier et al.^{46,51} provided evidence by HRTEM that deactivation of their composite system was governed by leaching of metallic Ni resulting in hollow NiO_x shells, or oxidation of Ni resulting in the formation of NiO_x particles (Figure 6.4). Evidently, in this system Ni serves as sacrificial reagent triggering the formation of hydrogen during illumination. In summary: it is evident that the simple model of static co-catalysts cannot describe the behavior, either under illumination or in the dark.

Logically, also for other co-catalyst systems, and especially complex materials like the common Rh/Cr₂O₃ core-shell co-catalysts, dynamic rearrangement during initial testing or prolonged illumination might occur. In fact, chromium oxide/oxyhydroxide films used in the chlorate process are usually considered as being dynamic in nature. Here, it is also interesting to note the following: 1) mixed metal (oxide) co-catalysts show comparable or even higher photocatalytic performances;^{4,52,53} 2) Cr₂O₃ shells are less effective in suppressing the back reaction of H₂ and O₂ when applied on Pt metal particles, suggesting that a simple description of CrO_x shells on metallic particles is not sufficient to describe the co-catalyst material.^{52,54}

6.3 Learning from other disciplines

Concerning the purpose of a co-catalyst, e.g. facilitating redox reactions at the semiconductor surface, guidelines to the design, stability, and understanding of active sites can be found in electrocatalysis (ignoring the semiconductor/electrocatalysts interface). Typically, in electrocatalysis, activities and stabilities of an electrocatalyst are addressed by voltammetry and chronoamperometric/-potentiometric measurements. Subsequent or even in-situ surface characterization is used to obtain structure-activity relations. Leaching and corrosion are investigated by determining metal contents in the used electrolyte. The number of active sites is precisely estimated by the materials weight, or the number of electrochemically active surface sites. In fact, certain protocols are established to ensure a practical description of materials and the reproducibility of obtained results.^{55–57} Similar protocols might be required in photocatalysis. For example in electrocatalysis, and especially for oxygen evolution, it is known that pseudo-stability during long-term testing can be achieved by providing a sufficient amount of electrocatalytically active material.⁵⁶ In these cases corrosion currents might be significantly smaller than currents generated due to the gas evolving reaction, and monitoring mass losses or detecting dissolved material in the electrolyte is a necessity.⁵⁶ It is also known that corrosion of noble metals such as Pt or Ir occurs during potential cycling, by successive oxidation and reduction of the surface.^{58–60} Time scales of corrosion might be different between electro- and photocatalysis due to

different proton/hydroxyl concentrations of the electrolyte, but a local pH gradient might still facilitate corrosion. A first indication of materials properties in different electrolyte conditions can be obtained using Pourbaix diagrams.

Just recently, along with the development of appropriate in-situ techniques, such as high-pressure XPS, changes in the oxidation state of NiO_x and IrO_2 OER catalysts were revealed during electrochemical oxygen evolution.^{61–64} For example, for Ir-based OER materials it is commonly observed that amorphous phases possess higher activities than their crystalline counterparts: the reasoning behind this observation is still a matter of speculation. Studying the oxidation state of Ir during OER using X-ray photoemission and absorption spectroscopy, Schloegel et al. were able to determine that 1) metallic Ir converts into a mixed-valence, conductive iridium oxide matrix, and 2) active sites in amorphous iridium oxide are likely composed of a weakly bound oxygen, susceptible to nucleophilic attack. Furthermore, the authors point out that a dynamic framework is required to allow flexibility in the oxidation state of Ir, which is required for the formation of oxygen.^{61,62}

Another interesting material known to change oxidation states during catalysis is NiO_x . The exact nature of the active site is still under debate. An interesting observation that needs to be highlighted is that incooperation of Fe-traces into the NiO-matrix results in dramatically improved OER capabilities.^{65,66} Similar observations were also reported for Co- and Mn-based materials, highlighting the importance of contaminants in applied electrolytes. For photocatalytic systems a proper understanding of the effect of metal-traces in electrolytes is even more important as, in contrast to electrochemical applications, co-catalysts quantities are typically small, and functional changes by contaminant incorporation will be expressed more dramatically.

Peculiar observations that might be of interest can also be found in electrochemical literature discussing effects of Cr-oxide films used to obtain electrochemical selectivity.^{29,30} Generally, Cr-oxide films are reported to increase the electrochemical selectivity of the hydrogen evolution reaction. Interestingly, Cr-oxide films are also reported to influence the activity of a hydrogen evolution catalysts. For example, for Pt@CrO_x materials slightly

higher overpotentials are measured for hydrogen evolution as compared to un-protected Pt. For Au-based materials, however, Cr-oxide films appear to positively influence the HER performance, suggesting different functions of the Cr-oxide film depending on the metal substrate. The effect of Cr-oxide is not yet fully understood in electrochemical systems; similarly the basic model of a core covered by a Cr-shell where the shell solely inhibits the backreaction might underestimate the role of Cr-oxide in photocatalysis.

As in the field of photocatalysis, major attention has been paid to the development of suitable semiconductor materials in photo-electrochemistry. Indeed, significant progress has been made in understanding and engineering semiconductor/co-catalyst interfaces.⁶⁷ For example, selective charge carrier contacts deposited between semiconductor and electrocatalyst were shown to dramatically improve the separation efficiencies and stabilities of PEC photoelectrodes.^{67,68} A feasible hole storage/extraction layer reported by the group of C. Li is MoO_x .⁶⁸ Given that MoO_x and CrO_x films possess similar charge carrier transport properties, MoO_x and CrO_x might serve similar purposes in composite photocatalysts.^{69,70} However, it will be a major challenge to utilize selective contacts on the nanoscale, and only locally on semiconductor particles. Nevertheless, the results obtained in PEC are encouraging and similar approaches should be followed in heterogeneous photocatalysis.

Another interesting concept towards improved understanding of semiconductor/co-catalysts interfaces was presented by Boettcher et al.⁷¹ They showed that ion-permeable catalysts such as Co-Pi and NiOOH, form adaptive Schottky-junctions with the semiconductor surface. Adaptive junctions change in-situ with the oxidation level of the co-catalysts, leading to improved performances compared with dense co-catalysts. Given the porous nature of e.g. NiO_x or chromium oxide films, the adaptive junction concept will also be applicable in photocatalysis.

Finally, knowledge developed in heterogeneous catalysis should be considered for composite catalysts design. Heterogeneous catalysts are composed of a support (e.g. an oxide such as silica or alumina) on which well-dispersed metallic nanoparticles with (ideally) a narrow size-distribution are deposited. In

photocatalysis, however, size distributions receive relatively little attention, and loading is solely optimized according to the relationship depicted in Figure 2. Co-catalysts of different sizes will develop different semiconductor/co-catalyst interfaces, as recently shown by Takanabe et al.⁹ Accordingly, the effectiveness of electron-transfer to the co-catalyst and the shift of the chemical potential, i.e. the potential required to drive the redox-reaction, will depend on particle size. Furthermore, stability issues and transition in oxidation states are likely particle size dependent and are difficult to investigate using a random arrangement of co-catalyst particles on the surface. One example indicating the feasibility of creation of particles in a narrow size range was recently reported by Li et al.⁷² Well-dispersed Pd nanoparticles were deposited on solid solutions of GaN:ZnO using atomic layer deposition (ALD). Remarkably, only 0.13 wt% Pd were required to obtain optimized functionality of the semiconductor.

Charge transfer and the subsequent shift of the chemical potential can be followed using Infrared spectroscopy and carbon monoxide probe molecules, as recently shown by Domen et al.¹² The potential shift is clearly averaged over all metallic particles deposited, and differences between particles might exist. Still these results evidence that a better understanding of co-catalysts can be developed utilizing suitable characterization techniques.

Multicomponent catalysts are also frequently applied in industrial heterogeneous catalysis: the different functions of the individual components cause improved performance and stability, and as depicted above for photocatalytic water splitting especially the stability (see leaching of Ni in the case of Ni/NiO) might be important. In this respect, it should be mentioned that recently a quaternary system consisting of Cr-, and Mo-oxide together with either Rh or CuO_x were applied for POWS showing improved water splitting behavior and stabilities.^{70,73}

In heterogeneous catalysis it is known that as-prepared materials are converted to the actual active catalyst primarily during initial stages of catalytic testing. For example, changes that might occur are particle sintering and Ostwald ripening^{74–76}, or even encapsulation of metallic particles by thin sub-stoichiometric oxides.⁵⁵ An important parameter in heterogeneous catalysis is

the turnover frequency (TOF), defining the reactivity per exposed surface site per unit of time. While it is important to note that the concept of TOF is not applicable to compare different heterogeneous photocatalysts and a high TOF is *not* a requirement for high photocatalytic efficiency, comparing TOFs calculated for fresh and used photocatalysts will underline changes occurring during reaction, e.g. by dissolution of the co-catalyst or changes in the interfacial properties between the co-catalyst and the semiconductor. In electrocatalysis TOFs are potential dependent and due to the perquisites of photocatalysis TOF numbers will provide indications of the generated potentials within the semiconductor and the quality of the (averaged) semiconductor/co-catalyst interface (considering a similar dispersion of the co-catalyst). Though the number of surface active sites on the semiconductor photocatalyst is difficult to define, advanced characterization methods, such as high-resolution X-ray photoelectron spectroscopy or low-energy Ion scattering, allow for a good estimate, e.g. of the number of available metallic sites for HER. Thus, TOF numbers (and the required materials characterization) might add additional fundamental understanding to describe the behavior of heterogeneous photocatalysts.^{77,78} Still it is important to report (STH) or quantum efficiencies (QE) for comparison of different heterogeneous photocatalysts. These values should be reported for the individually optimized system, i.e. optimized photocatalyst amount as well as optimized co-catalysts loading. For further information about the definition of these values the reader is referred to IUPAC conventions and existing literature.^{6,79}

As depicted by the examples mentioned above from electrochemistry and heterogeneous catalysis, utilizing existing knowledge of other disciplines is beneficial for the development of heterogeneous photocatalyst systems.

6.4 Points for improvements in co-catalyst development

A fair comparison of photocatalytic activities obtained in different laboratory's is complicated by differences in reactor type and irradiance (light intensities and lamps). Changes in pH and/or temperature will also significantly influence activities.⁷⁹ These issues have already been recognized, and reporting of

photocatalytic activities should always include a precise description of the process parameters and conditions, such as changes in pH during reaction.

Still it appears to be difficult to reproduce photocatalytic data mainly due to the complexity of materials. Common semiconductor materials are well-characterized, but significant progress is required in the description and characterization of co-catalysts. Modification of semiconductor surfaces is non-trivial, and yet it is not known whether conventional methods such as impregnation or other techniques, such as photodeposition⁸⁰, are preferable. Independent of the preparation techniques, it is important to realize that co-catalysts will likely *be in a dynamic state during reaction, and analyzing active sites during reaction is essential*. These dynamics should be revealed by advanced characterization techniques, preferably in operando conditions.

Furthermore, it should be considered that semiconductor particles have a heterogeneous surface structure, resulting in various exposed facets and surface defects. Defects and interfacial energy levels are regularly discussed in terms of recombination losses occurring during charge separation and transport, however, the surface heterogeneity will also result in different semiconductor co-catalysts interfaces, that will likely cause different (dynamic) states or even result in non-active “spectators”. Such spectators on the surface can even be detrimental and decrease the efficiency of light absorption by the semiconductor. Besides a few studies, co-catalyst loadings used in photocatalytic research are relatively large^{81,82} and it is arguable that these loadings can be reduced when positioned at appropriated places/facets on the semiconductor surface.

The required co-catalyst loading is even more important when water reduction and water oxidation electrocatalysts are simultaneously applied (co-loading) on a single semiconductor surface.⁸³ While co-loading might improve charge separation efficiencies and surface catalysis, the complexity of the system increases dramatically. Here, it is also of interest to develop suitable strategies to achieve selective contacts and facilitate the required electron and hole transfer processes towards the respective co-catalysts.

Non-noble metal-based materials are interesting, alternative co-catalysts. Generally, non-noble metal materials possess good activities for the forward H_2 evolution reaction and good electrochemical selectivity is expected as non-noble metals are usually poor catalysts to drive thermal recombination of hydrogen and oxygen, or the electrochemical reduction of oxygen. In these cases the use of complex core-shell structured materials will be redundant.^{69,84–86} From PEC studies it is even known that catalysts such as Mo_2C ⁸⁷, MoS_x ^{87,88} and other transition metal oxides⁸⁹ are suitable to achieve stable PEC performances. Most of these non-noble materials possess semiconducting properties⁹⁰ which will change the description of the semiconductor/co-catalyst interface. Unfortunately, from electrocatalysis it is also known that non-noble materials usually require higher overpotentials increasing the necessary chemical potential of electrons to drive the redox reaction. Also higher mass-loadings might be mandatory¹⁹ that in-turn are detrimental in photocatalytic applications.

The above mentioned phenomena showcasing the transformation of applied co-catalysts are not yet fully understood, and it is worth emphasizing that additional efforts to develop new co-catalysts, and better understand the behavior of currently applied co-catalysts systems is required. Understanding is particularly important, and crucial to design of composite heterogeneous photocatalysts that are able to drive solar-fuel generating reactions. It appears to be important to include descriptors and knowledge developed in electrocatalysis, photoelectrocatalysis, and heterogeneous catalysis including the various advanced (in-situ/operando) characterization techniques that are nowadays applicable for characterization of developed materials.^{11,78,85} In this respect a very recent study using in situ X-ray absorption spectroscopy indicates that the physico-chemical state of co-catalyst is significantly affected by light and surrounding electrolyte, leading to substantial difference in photocatalytic activity. Specifically it is suggested to consider the following when using co-catalysts.

First, co-catalyst development should be guided by a rational approach focusing on an effective charge transfer from the semiconductor to the co-catalyst to facilitate chemical potential shifts. Clearly random deposition of co-catalysts should be avoided, and photodeposition could be a means to selectively deposit

metal nanoparticles on desired surface locations. Understanding of the interfacial phenomena during photodeposition is also necessary.

Second, optimization of particle sizes, dispersion and loading must be performed individually for every semiconductor composition. We suggest the optimized co-catalyst system is strongly depending on the applied semiconductor.

Third, understanding of co-catalysts functionality requires detailed characterization. Characterization should be performed before and after catalytic testing and preferably *in-situ* (see for example recent efforts in electrocatalysis). Detection of ions dissolved in solution after catalytic testing is indicative of co-catalysts instability.

Fourth, an approach to facilitate better understanding might be the use of differentially operated reactor systems, in addition to the conventional recirculating batch reactors. These systems will allow reliable probing of the stability and activity of photocatalyst composite materials. Essential information, applicable to the development of heterogeneous photocatalysts, might be obtained during initial stages of testing.

6.5 Abbreviations

POWS, photocatalytic overall water splitting; STH, solar-to-hydrogen; SMSI, strong metal-support interactions; HER, hydrogen evolution reaction; HRTEM, high-resolution transmission electron microscopy; PDD, Pulsed Discharge Detector; TOF, turnover frequency; AQE, apparent quantum efficiency; ALD, atomic layer deposition.

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Chapter 7

Summary and perspective

Solar driven water splitting is considered a promising way to produce renewable energy-based resources. Among other materials, SrTiO_3 has previously been shown to be capable of driving photocatalytic overall water splitting. Usually the advantages of SrTiO_3 are summarized by the following: i) SrTiO_3 is a earth-abundant and non-toxic material with good stability under illumination; ii) it has a suitable band gap to allow for solar light absorption and the positions of the valence and conduction band straddle the thermodynamic redox potentials of water reduction and oxidation; iii) the typical ABO_3 structure allows for modification of its electronic structure by substituting the metal cations in A or B position. In this thesis, SrTiO_3 is also used as the photocatalyst for water splitting. Due to these benefits, SrTiO_3 is also used as the light absorbing material/photocatalyst in this thesis. Several strategies have been applied to understand particular functions of the SrTiO_3 -based photocatalyst and improve the performance for POWS. Surface modification by Ni/NiO co-catalysts is shown to improve reaction kinetics, the incorporation of Mg into the SrTiO_3 bulk is shown to increase charge separation and the deposition of CrO_x allows for improvements in photocatalyst stability. Generally, the effect of the various modifications on the photocatalytic gas evolution rates has been revealed by reliable on-line GC measurements. Due to the fast detection mode of the GC, the applied setup allows to determine transients in gas-evolution to reveal activity and stability of the tested photocatalysts. In the following the individual chapters are shortly summarized, before several recommendations are given. In contrast to chapter 6, the outlook and the recommendations are more specific. Here recommendations are given providing guidelines to further progress the development and understanding of, in particular SrTiO_3 -based, photocatalysts for overall water splitting.

In chapter 2, surface modification of SrTiO_3 is achieved by deposition of core/shell Ni/NiO structures. The performed photocatalytic water splitting measurements show that the composite 1) produces non-stoichiometric product mixtures and 2) continuously deactivates. With the help of TEM and XPS measurements, the transients in hydrogen evolution rates, and corresponding morphological changes of Ni/NiO core-shell particles are explained by the in situ formation of NiOOH upon illumination. Moreover, the metallic Ni core is

proposed to serve as sacrificial agent in the water splitting process, and during regeneration. Theoretically, the photocatalytic reaction should stop when all the Ni is sacrificed. Certainly long term experiments and in-situ studies are required to further explore the dynamic behavior of Ni/NiO core/shell co-catalysts.

In chapter 3, a simple two-step solid state method has been described to prepare Mg-modified SrTiO_3 photocatalysts. As shown by XRD and Raman characterization, variation of Mg-content results in materials consisting of various phases. Only for a stoichiometric ratio of (Mg+Ti):Sr, phase pure Mg:SrTiO₃ materials are obtained. After deposition of Ni/NiO or Pt co-catalyst, the synthesized materials show dramatic improvement in the photocatalytic overall water splitting (POWS) rates compared to unmodified SrTiO₃. Among all the Mg-modified SrTiO₃ samples, pure ABO₃-phase type of Mg:SrTiO₃ provides the highest steady-state apparent quantum yield of 9.1% (based on a range of 300-400 nm solar light illumination). Still significant deactivation during the initial hours of illumination is observed likely due to a similar rearrangement of the co-catalyst as discussed in chapter 2. Mott-Schottky measurements and photocatalytic reactions in the presence of sacrificial agents indicated that the beneficial effect of Mg is due to an extension of the depletion layer (from 25 to 50 nm), allowing for better oxygen evolution. The results also indicate that the electron transfer to the surface is limited and the presence of an appropriate interface with a hydrogen evolution catalysts is of importance. It needs to be emphasized that Mg is most probably leaching out of the photocatalyst during washing. Still, as observed later (chapter 4), leaching also occurs during pre-conditioning (reactor purging overnight), so the Mg content in the material must be verified at different steps of the photocatalytic water splitting procedure. Also, further measurement needs to be conducted to fully reveal how Mg is incorporated in the SrTiO₃ structure.

In chapter 4, Cr₂O₃ is photodeposited on NiO_x modified SrTiO₃ and Mg:SrTiO₃ materials. TEM and TEM-EDX measurements indicate that Ni and Cr are well distributed on the surface. Furthermore, photocatalytic measurements reveal that an apparent quantum efficiency of 30% is obtained for the Mg:SrTiO₃-NiO_x-Cr₂O₃ catalyst under 365 nm LED light illumination. The increase is assigned to an improved stability of the material. The stability is preserved for at least 70

hours. CrO_x is usually reported to be a protective layer used to prevent the back reaction of formed H_2 and O_2 . However, for the $\text{Mg}:\text{SrTiO}_3\text{-NiO}_x\text{-Cr}_2\text{O}_3$ catalyst, this is only of minor importance. The analysis of the reaction solution by ICP at different stages of the photocatalytic process reveals that Cr_2O_3 prevents both Mg and Ni from leaching to the solution, in turn improving the stability of the material and maintaining its outstanding photocatalytic properties. A detailed investigation to understand the mechanism preventing leaching of Mg and Ni still has to be performed, particularly as the most recent result (in-situ ICP analysis) also indicate leaching of Sr is significant.

In chapter 5, a comparative performance analysis of two emerging semiconductor materials, namely $\text{Al}:\text{SrTiO}_3$ and $\text{Mg}:\text{SrTiO}_3$, is performed. The direct comparison of materials prepared in different laboratories ($\text{Al}:\text{SrTiO}_3$ prepared in the group of F. Osterloh, UC Davis) highlights the importance of reaction conditions when comparing photocatalyst efficiencies. As shown, the photocatalytic performance of both materials, $\text{Al}:\text{SrTiO}_3$ and $\text{Mg}:\text{SrTiO}_3$, is very similar, but their individual optimal activity is obtained at slightly different reaction conditions, e.g. photocatalyst concentrations. The measurable difference in their individual optimal efficiency might due to the difference in materials' light absorption and particularly in the properties of the dispersion of the particles. Further work has to be done to fully reveal the light distribution within the reactor and in-situ measurements of the absorption and scattering behavior of the two different semiconductors must be performed.

Finally in chapter 6, recent literatures based on frequently applied co-catalysts (Pt, Rh/ Cr_2O_3 or Ni/NiO) systems are summarized, discussed and similarities with other fields of research and necessary advances in the field are outlined, especially in the development of a better understanding of co-catalyst/semiconductor interfaces.

The research work in this thesis has focused on core/shell Ni/NiO co-catalyst modified SrTiO_3 in photocatalytic overall water splitting with following aspects: i) the photocatalytic transients are collected to understand how Ni/NiO co-catalyst is changed during illumination; ii) Mg is doped into the structure of SrTiO_3 to improve the photocatalytic activity; iii) Cr_2O_3 is introduced on

Mg:SrTiO₃-NiO_x composite to improve the stability of photocatalytic gas evolution; iv) state-of-the art semiconductors, Al:SrTiO₃ and Mg:SrTiO₃, are compared in the same conditions. Thus, the research summarized in this thesis was generally guided by limitations in the performance of the photocatalysts. However, several questions still remain to be answered and even new interesting research questions can be formulated based on the most recent findings (summarized in chapter 4 and chapter 5):

i) as indicated by in-situ ICP-MS measurements leaching of strontium, magnesium and nickel occurs during pre-conditioning (reactor purging) and testing of the various photocatalyst formulations. In particular the leaching of Sr is interesting and should be studied in more detail. SrTiO₃ is usually considered to be stable within a wide range of pH and electrochemical potential, though it is also reported that selective etching of the surface/removal of SrO or TiO layers can be achieved. For the preparation of a photocatalyst with long-term stability leaching should be suppressed. Thus, it is suggested to study selective removal of SrO/TiO surface layers, and analyze the effect on photocatalytic performance. Certainly, a detailed characterization (XRF, ICP and TEM) by needs to be performed to obtain structure-activity relationships;

ii) the exact positioning of Mg within the structure of Mg:SrTiO₃ still needs to be revealed, and it is suggested to revisit the synthesis procedure of Mg:SrTiO₃. So far high temperature treatment has been performed at 1100 degrees at a constant time. The parameters have been chosen to match the procedure used for unmodified SrTiO₃. Still it appears likely that the synthesis procedure, i.e. the driving force for Mg and Sr incorporation into the TiO₂ lattice, is influenced by the temperature treatment and used precursors and in turn strongly influences the properties of the photocatalyst;

iii) during photocatalytic measurements for various materials deposition on the wall or in the corners of the photoreactor occurred, strongly influencing the dispersion. Re-designing of the reactor or testing of thin film materials might circumvent this problem. Apart from the mentioned stability problems, it is important to obtain a illumination profile for the photoreactor currently in use, to ensure a reliable evaluation of tested photocatalyst;

iv) the modification of the semiconductor surfaces by co-catalysts, e.g. Ni/NiO, results in a random deposition/dispersion of co-catalyst on the semiconductor surface. In fact it appears to be important that co-catalyst deposition is performed site-selective and probably with well-defined inter-particle distances. The semiconductor surface is usually considered to be homogeneous in nature, however, various surface terminations and a large number of surface defects are present that might affect the interaction with co-catalysts (formation of ohmic contacts vs. Schottky barriers). The interface between co-catalyst and semiconductor will affect the physical/chemical state, which consequently influences the surface reaction. To fully reveal the potential of a semiconductor, such as Mg:SrTiO₃, this has to be taken into account. Fundamental studies with advanced characterization techniques of high spatial resolution accompanied by relevant modelling of the surface are required to understand the co-catalyst/semiconductor interface effect.

v) for the half reaction (O₂ evolution with Fe₂(SO₄)₃ as the sacrificial agent), O₂ production rates of 2 μmol·g⁻¹·mol⁻¹ was obtained with the pristine Mg:SrTiO₃ photocatalyst. The maximum O₂ evolution rate obtained for Mg:SrTiO₃-RhCrO_x during overall water splitting system is limited to about 1.6 μmol·g⁻¹·mol⁻¹. Thus, further improvements of the photocatalytic performance of this material are still feasible. As the limitation is likely governed by the co-catalyst the synthesis procedure, see above, should be revised. Furthermore, it is suggested that combination such as recently reported modifications of RhCrO_x by MoO_x, or the use of additional protection layer, such as TiO₂ layer will help to obtain the full potential of Mg:SrTiO₃ photocatalysts.

vi) Considering the reported synthesis method of CrO_x-modified Ni/NiO co-catalysts it is also important to mention that a detailed investigation has not yet been performed. Currently Ni/NiO co-catalysts are prepared in a standardized way. It is, however, known that the thickness of the NiO shell and the diameter of the Ni core can be easily tuned by time and temperature of the required heat-treatment. Modulating the thickness of the NiO shell before photodeposition of CrO_x might further improve the stability/activity of the co-catalyst by a preferred interaction of CrO_x and the Ni/NiO core-shell structure.

Apart from the recommendations summarized above several other suggestions can be formulated when considering the applicability of Mg:SrTiO_3 on industrial scale. Generally, it is reported that the solar-to-hydrogen (STH) efficiency must exceed 10% to be competitive with traditional industrial process, like methane steam reforming. However, the STH efficiencies of all materials are still far behind the applicable efficiency, especially for traditional photocatalysts system, where single absorber materials are dispersed in water, and an STH below 1% is usually reported. General suggestions are the following:

In first instance the absorption properties, i.e. the band gap, of a semiconductor material determines the STH that can be theoretically achieved. For SrTiO_3 absorption of solar light is restricted to the UV-part of the light spectrum limiting its theoretical STH to be approx. 1.5 %, while the obtained maximum in our system is 0.1%. Considering the STH measured for the systems reported in this thesis even with SrTiO_3 -based materials significant improvements can still be achieved. However, to achieve the targeted values a suitable semiconductor with an absorption edge at 600 nm and appropriate VB and CB positions must be developed. Strategies to modify the band gap of SrTiO_3 involve – doping with transition metals (Rh, Cr, or V) or anion (N, S, C) doping. Given existing literature reporting on the effect of doping it is, however, doubted that doping will solve the above mentioned issues. Thus, semiconductor development guided by theoretical calculations is required. Besides, integration with other visible light absorbing materials in a Z-scheme like configuration is of interest to achieve required STH efficiencies. Finally, it must be mentioned that the development of industrial applications is usually guided by a techno-economical evaluation of a process, where initial investments and return of investment will provide guidelines for product prices. Assuming high AQY under monochromatic illumination, such as LED illumination, a light-to-light to product process might be of interest, Although, a detailed techno-economic evaluation is required, low costs of solar cells, efficient LED illumination and low semiconductor prices might favor such an approach.

Hoofdstuk 7

Samenvatting en perspectief

Zonlicht gedreven watersplitsing wordt beschouwd als een veel belovende manier om waterstof te maken met behulp van duurzame energie. Eerder is aangetoond dat het mogelijk is water volledig fotokatalytisch te splitsen over materialen zoals SrTiO_3 . De voordelen van SrTiO_3 worden meestal als volgt samengevat: i) SrTiO_3 is een op aarde veel voorkomend en niet schadelijk materiaal met een goede stabiliteit onder belichting; ii) Het heeft een passende bandkloof voor de absorptie van zonlicht, en de posities van de valentie- en geleidingsband bestrijken de thermodynamische redoxpotentialen voor waterreductie en -oxidatie; en iii) de typische ABO_3 structuur maakt het mogelijk om de elektronische structuur aan te passen door vervanging van de metaalkationen in de A of B positie. Het is vanwege deze voordelen dat SrTiO_3 ook in dit proefschrift als lichtabsorptiemateriaal/fotokatalysator wordt gebruikt. Verschillende strategieën zijn gebruikt om de specifieke functies van de op SrTiO_3 gebaseerde fotokatalysator te begrijpen en de prestaties met betrekking tot volledige fotokatalytisch watersplitsing te verbeteren. Door het oppervlakte te veranderen met Ni/NiO co-katalysatoren is te zien dat de reactiekinetiek verbeterd, het inbouwen van Mg in de SrTiO_3 bulk laat een toename in de ladingscheiding zien en de afzetting van CrO_x zorgt voor verbeteringen in de fotokatalytisch stabiliteit. In het algemeen zijn de effecten van deze verschillende aanpassingen op de snelheid van fotokatalytisch gasontwikkeling in kaart gebracht met behulp van betrouwbare gaschromatografiemetingen. Dankzij de snelle detectiemogelijkheid van de GC kunnen met de gebruikte opstelling kortstondige ontwikkelingen in gasontwikkeling worden bepaald, welke inzicht geven in de activiteit en stabiliteit van de geteste fotokatalysatoren. In het hierop volgende worden de individuele hoofdstukken kort samengevat, voordat enkele aanbevelingen worden gegeven. In tegenstelling tot hoofdstuk 6 zijn de vooruitblik en de aanbevelingen hier specifieker. Er worden aanbevelingen gegeven die als richtlijn dienen voor verdere vooruitgang op het gebied van de ontwikkeling en het begrip van, voornamelijk op SrTiO_3 gebaseerde, fotokatalysatoren voor het volledig splitsen van water.

In hoofdstuk 2 is het oppervlak van SrTiO_3 aangepast door er Ni/NiO-kern/schilstructuren op af te zetten. De uitgevoerde fotokatalytische

watersplitsingsmetingen tonen aan dat het composiet; 1) niet stoichiometrische productmengsels geeft en 2) voortdurend deactiveert. Met behulp van TEM en XPS metingen worden de veranderingen in waterstofproductiesnelheid en corresponderende veranderingen in de morfologie van Ni/NiO kern/schil deeltjes uitgelegd aan de hand van in-situ NiOOH formatie tijdens belichting. Verder wordt voorgesteld dat de metallische Ni kernen worden gebruikt in het watersplitsingsproces, en tijdens de regeneratie.

In hoofdstuk 3 wordt een eenvoudige tweetraps vastestofchemiemethode beschreven voor de bereiding van Mg-gemodificeerd SrTiO₃ fotokatalysatoren. Uit XRD en Raman karakterisering blijkt dat variatie in de hoeveelheid Mg leidt tot materialen met meerdere fasen. Alleen voor een stoichiometrische verhouding van (Mg+Ti):Sr worden materialen van een pure Mg:SrTiO₃ fase verkregen. Na het afzetten van de Ni/NiO of Pt co-katalysator laten de gesynthetiseerde materialen een dramatische verbetering zien, ten opzichte van het onaangepaste SrTiO₃, in de snelheid waarmee water fotokatalytisch wordt gesplitst. Van alle met Mg-gemodificeerde SrTiO_x fotokatalysatoren, blijkt het type Mg:SrTiO₃ van het type met een zuivere ABO₃-fase het hoogste ogenschijnlijkkwantumrendement te laten zien in stationaire toestand (9.1% op basis van een 300-400 nm spectrum onder belichting met zonlicht). Desondanks wordt nog steeds een aanzienlijke deactivatie gezien gedurende de eerste uren van belichting. Waarschijnlijk komt dit door een herstructurering van de co-katalysator, wat vergelijkbaar is met hetgeen wat is besproken in hoofdstuk 2. Mott-Schottky-metingen en fotokatalytische reacties in de aanwezigheid van opofferingsreactanten wijzen erop dat het gunstige effect van Mg, waardoor de zuurstof ontwikkeling beter verloopt, resulteert uit het verdiepen van de onderbezette laag (van 25 naar 50 nm). Dit resultaat wijst er ook op dat de elektronoverdracht naar het oppervlak limiterend is, en de aanwezigheid van een geschikt grensvlak met een waterstofkatalysator van belang is. Het dient te worden benadrukt dat het zeer aannemelijk is dat Mg uit de fotokatalysator loopt tijdens het wassen. Bovendien, zoals later waargenomen (hoofdstuk 4), vind uitloggen ook plaats tijdens de voorbereiding (het doorblazen van de reactor gedurende de nacht), hierom dient de hoeveelheid Mg in het materiaal geverifieerd te worden bij iedere stap in de procedure voor het fotokatalytisch

splitsen van water. Tevens zullen verdere meting moeten worden uitgevoerd om volledige duidelijkheid te verschaffen over hoe Mg daadwerkelijk in de SrTiO_3 structuur zit verwerkt.

In hoofdstuk 4 wordt Cr_2O_3 doormiddel van fotodepositie op, met NiO_x gedecoreerd, SrTiO_3 en Mg:SrTiO_3 materialen afgezet. TEM en TEM-EDX metingen duiden erop dat Ni en Cr goed over het oppervlak verspreid zijn. Verder laten fotokatalysmetingen zien dat een ogenschijnlijk kwantumrendement van 30% wordt behaald voor de Mg:SrTiO_3 - NiO_x - Cr_2O_3 katalysator onder belichting met een 365 nm LED. De stabiliteit is gewaarborgd tot minimaal 70 uur. Gewoonlijk wordt het gebruik van CrO_x gerapporteerd als een beschermende laag, welke de terugreactie van het gevormde H_2 en O_2 voorkomt. Echter is dit voor de Mg:SrTiO_3 - NiO_x - Cr_2O_3 katalysator slechts van klein belang. Er blijkt namelijk uit de analyse van de oplossing waarin de reactie plaats vindt doormiddel van ICP, op verschillende momenten in het fotokatalytische proces, dat Cr_2O_3 voorkomt dat Mg en Ni de oplossing inlogen. Met als gevolg een materiaal met verbeterde stabiliteit en uitstekende fotokatalytische eigenschappen. Een diepere studie in het begrijpen van het mechanisme dat het uitloggen van Ni en Mg voorkomt moet nog worden gedaan, voornamelijk omdat het meest recente resultaat (uit in-situ ICP-analyse) ook wijst op een significante uitloging van Sr.

In hoofdstuk 5 worden de prestaties van twee opkomende halfgeleidermaterialen vergeleken, Al:SrTiO_3 en Mg:SrTiO_3 . De directe vergelijking tussen de materialen, gemaakt op verschillende laboratoria (Al:SrTiO_3 gemaakt in de groep van F. Osterloh, UC Davis), stipt het belang van de reactiecondities aan wanneer fotokatalytische efficiëntie wordt vergeleken. Zoals aangetoond zijn de fotokatalytische prestaties van de beide materialen, Al:SrTiO_3 en Mg:SrTiO_3 , zeer vergelijkbaar. Echter wordt de optimale efficiëntie van deze materialen elk bij iets andere condities bereikt, zoals bijvoorbeeld een andere concentratie van de fotokatalysator. De gemeten verschillen tussen de individuele efficiëntieoptima zouden het gevolg kunnen zijn van verschillen in licht absorptie eigenschappen van de materialen en dan specifiek wanneer de deeltjes gedispergeerd zijn. Verder onderzoek is nodig om volledig te laten zien hoe licht zich verdeelt in de reactor en in-situ metingen

van het absorptie- en verstrooiingsgedrag van de twee verschillende halfgeleiders moeten worden uitgevoerd.

Tot slot wordt in hoofdstuk 6 de recente literatuur met betrekking tot veel gebruikte co-katalysator systemen (Pt, Rh/Cr₂O₃ of Ni/NiO) samengevat, bediscussieerd en overeenkomsten met andere onderzoekslijnen en de vereiste vooruitgang in het werkveld worden uiteengezet, met nadruk op de ontwikkeling van een beter begrip van het co-katalysator/halfgeleider-contactvlak.

Het onderzoek in dit proefschrift is in het algemeen geleid door de gelimiteerde prestaties van de fotokatalysatoren. Er zijn echter nog verscheidene vragen die beantwoord moeten worden en zelfs nieuwe interessante onderzoeksvragen die geformuleerd kunnen worden op basis van de meest recente bevindingen (samengevat in hoofdstuk 5 en 6):

i) Zoals aangetoond met de in-situ ICP-MS metingen, vind het uitlogen van strontium, magnesium en nikkel plaats tijdens de voorbereiding (het doorblazen van de reactor) en het testen van de verschillende fotokatalysatoren. Nadrukkelijk is het uitlogen van Sr interessant en dient dit in meer detail bestudeert te worden. SrTiO₃ wordt over het algemeen als stabiel beschouwd in een breed pH en elektrochemisch potentiaal gebied, hoewel er ook is gerapporteerd over de mogelijkheid om selectief SrO of TiO lagen van het oppervlak te etsen /verwijderen. Voor de bereiding van een fotokatalysator met een langdurige stabiliteit zal uitloging moeten worden onderdrukt. Hierom wordt aangeraden om te kijken naar het selectief verwijderen van SrO/TiO oppervlaktelagen, en vervolgens het effect hiervan op de fotokatalytische presentaties te analyseren. Gedetailleerde karakterisering (XRF, ICP en TEM) zal nodig zijn om structuur-activiteitrelaties te verkrijgen.

ii) De exacte positionering van Mg binnen de structuur van Mg:SrTiO₃ moet nog worden opgehelderd, en het wordt geadviseerd om de syntheseprocedure van Mg:SrTiO₃ nog eens te bekijken. Tot dusver is de hoge temperatuurbehandeling uitgevoerd op 1100 K en is de tijd constante gehouden. Deze parameters zijn gekozen omdat ze overeenkomen met de procedure die wordt gebruikt om puur SrTiO₃ te maken. Toch lijkt het aannemelijk dat de

syntheseprocedure, i.e. de drijvende kracht voor inmenging van Mg en Sr binnen het TiO_2 rooster, wordt beïnvloed door temperatuurbehandeling en de gebruikte uitgangsstoffen. Dit beïnvloed vervolgens weer sterk de eigenschappen van de fotokatalysator.

iii) Tijdens fotokatalysemetingen voor verschillende materialen vond neerslag plaats op de wand en in de hoeken van fotoreactor, wat sterk de dispersie van de katalysator beïnvloed. Door het opnieuw ontwerpen van de reactor of het testen van dunne laag materialen zou dit probleem kunnen worden omzeilt. Behalve de genoemde stabiliteitsproblemen is het ook zaak om een lichtprofiel van de huidige reactor in kaart te brengen, dit om er zeker van te zijn dat de fotokatalysator betrouwbaar kan worden getest.

iv) De aanpassing van de halfgeleideroppervlakten met co-katalysatoren, e.g. Ni/NiO, resulteert in een willekeurige afzetting/spreiding van de co-katalysator op het halfgeleideroppervlak. Het blijkt echter van belang dat de co-katalysatordepositie plaats-selectief plaats vind en waarschijnlijk met een goed gedefinieerde afstand tussen de deeltjes. Het halfgeleideroppervlak word normaal gesproken beschouwd als van nature homogeen, echter zijn verscheidene oppervlakteterminaties en een grote hoeveelheid aan oppervlakte-defecten aanwezig welke mogelijk de interactie met de co-katalysator beïnvloeden (vorming van een ohms-contact tegenover Schottky-barrières). Het grensvlak tussen de co-katalysator en de halfgeleider zal van invloed zijn op de fysische/chemische toestand, dit heeft vervolgens weer invloed op de reactie aan het oppervlak. Om volledig inzicht te krijgen in het potentiaal van een halfgeleider, zoals Mg:SrTiO_3 , zal dit in overweging moeten worden genomen. Fundamentele studies met geavanceerde karakteriseringstechnieken en een hoge ruimtelijke resolutie, in combinatie met correcte modelering van het oppervlak, zijn nodig om de co-katalysator/halfgeleider-grensvlakeffecten te begrijpen.

v) Voor de O_2 -ontwikkelingshalfreactie (met $\text{Fe}_2(\text{SO}_4)_3$ als opofferingsreactant) zijn O_2 -productiesnelheden van $2 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{mol}^{-1}$ waargenomen met een zuivere Mg:SrTiO_3 fotokatalysator. De maximale O_2 -ontwikkelingssnelheid verkregen voor $\text{Mg:SrTiO}_3\text{-RhCrO}_x$ tijdens volledige watersplitsing is beperkt tot

ongeveer $1,6 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{mol}^{-1}$. Verdere verbeteringen van de fotokatalytische prestaties van dit materiaal zijn dus nog steeds mogelijk. Omdat de beperkingen waarschijnlijk worden overheerst door de syntheseprocedure van de co-katalysator, zie hier boven, zou deze moeten worden heroverwogen. Verder wordt gesuggereerd dat de combinatie van recentelijk gerapporteerde aanpassingen van RhCrO_x met MoO_x , of het gebruik van extra beschermende lagen, zoals TiO_2 , zullen helpen met het realiseren van het volwaardige potentiaal van Mg:SrTiO_3 fotokatalysatoren.

vi) Met in achtneming van de gerapporteerde synthesesmethode voor met CrO_x aangepaste Ni/NiO co-katalysatoren is het belangrijk om te noemen dat een gedetailleerd onderzoek nog niet is gedaan. Momenteel worden Ni/NiO co-katalysatoren bereid op een gestandaardiseerde manier. Het is echter bekend dat de dikte van de NiO -schil en de diameter van de Ni -kern makkelijk kunnen worden gevarieerd doormiddel van tijd- en temperatuurinstellingen van de vereiste hittebehandeling. Het afstellen van de NiO -schaaldikte voorafgaand aan de fotodepositie van CrO_x zou de stabiliteit/activiteit van de co-katalysator verder kunnen verbeteren door een gewenste interactie tussen de CrO_x en de Ni/NiO -kern/schilstructuur te weeg te brengen.

Afgezien van de adviezen die hier boven zijn samengevat kunnen ook enkele anderen suggesties worden gegeven met betrekking tot de toepasbaarheid van Mg:SrTiO_3 op een industriële schaal. In het algemeen wordt aangehouden dat de zonlicht-naar-waterstof (ZNW) efficiëntie boven de 10% moet liggen om competitief te zijn met traditionele industriële processen, zoals de stoomreforming van aardgas. Echter ligt de ZNW-efficiëntie van alle materialen nog verachter de toepasbare efficiëntie, in het bijzonder voor traditionele fotokatalysatoren waarbij een enkel absorptie materiaal is gedispergeerd in water en een ZNW-efficiëntie beneden de 1% normaal gesproken wordt gerapporteerd. Algemene suggesties zijn de volgende: Ten eerste de absorptie eigenschappen, i.e. de bandkloof, van het halfgeleidermateriaal bepaald de theoretisch haalbare ZNW-efficiëntie. Voor SrTiO_3 is de absorptie van zonlicht beperkt tot het UV gedeelte van het lichtspectrum, dit limiteert de theoretische ZNW-efficiëntie tot ongeveer 1,5%, terwijl het maximum dat is behaalt in ons systeem 0,1% is. Kijkend naar de ZNW-efficiëntie die zijn gemeten voor de

gerapporteerde systemen in dit proefschrift, zijn er nog significante verbeteringen mogelijk voor op SrTiO_3 gebaseerde materialen. Echter zal om de beoogde waarden te bereiken een passende halfgeleider met een absorptiegrens op 600 nm en de juiste valentie- en geleidingsbandpositie moeten worden ontwikkelt. Strategieën om de bandkloof van SrTiO_3 aan te passen zijn bijvoorbeeld dopen met overgangsmetalen (Rh, Cr en V) of anionen (N, S en C). Op basis van de bestaande literatuur over het effect van dopen lijkt het echter twijfelachtig of dopen daadwerkelijk de eerder genoemde problemen zou verhelpen. Hierom is halfgeleiderontwikkeling geleid door theoretische berekeningen een vereiste. Hiernaast is integratie van andere zichtbaar licht absorberende materialen in een Z-schema configuratie een interessante methode om de vereiste ZNW-efficiëntie te bereiken. Tot slot dient benoemd te worden dat de ontwikkeling van industriële toepassingen gebruikelijk wordt geleid door een techno-economische evaluatie van het proces, waarbij het investeringsrendement de richtlijn geeft voor de prijs van het product. Onder de aanname van een hoog ogenschijnlijkkwantumrendement met monochromatische verlichting, zou een licht-naar-licht-naar-product proces mogelijk interessant zijn. Hoewel een gedetailleerde techno-economische evaluatie een vereiste is, zouden lage kosten voor zonnecellen, efficiëntie LED belichting en lage halfgeleider prijzen een dergelijk aanpak kunnen begunstigen.

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Curriculum Vitae

Kai Han was born on April 1st 1989 in Jinan city, China. In 2011, he obtained his Bachelor degree in environmental engineering at Dezhou University in China. At the same year, he started his Master in applied chemistry at Dalian University of Technology in china. During his Master, he focused on integrating organic complexes with quantum dots for photocatalytic H₂ production. In June 2014, he obtained his Master degree from Dalian University of Technology. Since from 2014, he started his PhD in the Photocatalytic Synthesis Group at University of Twente in The Netherlands. The focus of his doctoral project is structural modification of semiconductor materials for the transformation of light into chemical energy by splitting water into oxygen and hydrogen.