CrOx-mediated Performance Enhancement of Ni/NiO-Mg:SrTiO3 in Photocatalytic Water Splitting

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Article

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Abstract

By photodeposition of small quantities of CrOx on SrTiO3-based semiconductors, doped with aliovalent Mg(II) and functionalized with Ni/NiO catalytic nanoparticles (economically significantly more viable than commonly used Rh catalysts), an increase in Apparent Quantum Efficiency (AQEs) from ~10% to 26% in overall water splitting was obtained. Deposition of CrOx also significantly enhances the stability of Ni/NiO nanoparticles in production of hydrogen, allowing sustained operation, even in intermittent cycles of illumination. In situ elemental analysis of the water constituents during, or after photocatalysis, shows that after CrOx deposition, dissolution of Ni-ions from Ni/NiO-Mg: SrTiO3 is significantly suppressed, explaining the stabilizing effect of CrOx on water splitting performance. State-of-the-art electron microscopy and EDX and EELS analyses demonstrate that upon preparation, CrOx is photodeposited in the vicinity of several, but not all, Ni/NiO particles. This implies the formation of a Ni-Cr mixed metal oxide, which is highly effective in water reduction. Inhomogeneities in the interfacial contact, evident from differences in contact angles between Ni/NiO particles and the Mg: SrTiO3 semiconductor, likely affect the probability of reduction of Cr(VI)-species during synthesis by photodeposition, explaining the observed inhomogeneity in the spatial CrOx distribution. Furthermore, by comparison with undoped SrTiO3, Mg-doping appears essential in providing such favorable interfacial contact and to establish the beneficial effect of CrOx. This study suggests that the performance of semiconductors can be significantly improved if inhomogeneities in interfacial contact between semiconductors and highly effective catalytic nanoparticles can be resolved by (surface) doping and improved synthesis protocols.

Introduction

The performance of SrTiO3 (STO) based photocatalysts in the light-driven overall splitting of water to H2 and O2 has recently been significantly improved by aliovalent doping of the perovskite material by Al or Mg, and surface-modification by deposition of appropriate co-catalysts such as Rh/CrOx.1–7 In fact for Rh/CrOx-modified Al:STO an apparent quantum efficiency (AQY) of up to 96% (UV-LED illumination) and solar to hydrogen efficiency (STH) of 0.65% have been reported.6 Triggered by this successful development, the first large scale flat-plate reactors are evaluated in long-term stability measurements under realistic conditions.7 The outstanding properties of aliovalently doped Al:STO have been assigned to removal (lower density) of Ti3+ mid-gap states (favorable recombination sites), which was recently confirmed by a combined experimental and theoretical investigation.4 Similarly, for Mg:STO composites (AQY of 10% promoted with Ni/NiO), some of us proposed that Mg reduces the density of free-charge carriers leading to a favorable surface-space-charge layer, promoting the oxygen evolution reaction.3 Still co-catalyst modification is mandatory to facilitate water reduction at the surface of these aliovalently doped SrTiO3-based composites. Particularly, co-catalysts consisting of chromium-oxide and typically Rh8–10 have been widely utilized to induce photocatalytic activity of SrTiO3 or Al:SrTiO3 photocatalysts. In this context CrOx is generally proposed to form thin film coatings on active hydrogen evolution catalysts, preventing the parasitic oxygen reduction reaction.6,8,11–13 Despite the frequently employed
picture of a core-shell structure, recent studies demonstrate that formation of mixed metal oxides containing CrO$_x$ and e.g. Rh, is also likely.$^{1,14,15}$

Ni/NiO co-catalysts are another type of often employed co-catalysts enabling photocatalytic overall water splitting. Similarly to CrO$_x$ in Rh/CrO$_x$, a NiO-shell is believed to prevent oxygen reduction to occur on the metallic Ni core.$^{16}$ Additionally, it has been reported that spatially separated particles of Ni and NiO$_x$ promote the formation of hydrogen and oxygen, respectively.$^{17,18}$ Recently, we revealed significant and unfavorable transients in the hydrogen production rate using Ni/NiO-modified SrTiO$_3$.$^{18}$ Dynamics in composition and structure of the Ni/NiO core–shell particles correlate well with the observed transients in gas evolution.$^{19}$ Certainly, stabilization of the active phase(s) of the Ni/NiO co-catalyst system is required to fully exploit the potential of the system, which is potentially more economically viable than Rh-based formulae.$^{19,20}$

Here, we report novel insight in the extent and origin of the effect of CrO$_x$ prepared by reductive photodeposition on unprecedented enhancement of the photocatalytic activity and stability of Ni/NiO$_x$-Mg:SrTiO$_3$ composite photocatalysts. High-resolution transmission electron microscopy with energy dispersive X-ray or electron energy loss spectroscopy (HR-TEM-EDX/EELS) reveals a spatial CrO$_x$ distribution primarily in the vicinity of the Ni/NiO$_x$ particles. The EDX and EELS data are explained by the formation of mixed CrO$_x$/NiO$_x$ phases. Moreover, (in-situ) Inductively coupled plasma mass spectrometry/optical emission spectrometry (ICP-MS/OES) illustrates a significant reduction in leaching/dissolution of Ni-ions from CrO$_x$/NiO$_x$ phases as compared to Ni/NiO$_x$ during cyclic operation. It will be discussed that Mg synergistically promotes the activity of the composite photocatalyst, likely by providing a favorable interfacial contact between the semiconductor (Mg:SrTiO$_3$) and the Ni/NiO$_x$ particles. The insights provided will guide research devoted to increasing performance, including stability, of photocatalysts.

**Experimental Methods**

**Materials**

SrTiO$_3$ was prepared by mixing and grinding of stoichiometric amounts of SrCO$_3$ (99.995 % Sigma-Aldrich) and Rutile TiO$_2$ (99.995% Sigma-Aldrich) and subsequent calcination at 1100 °C for 10 h. Mg:SrTiO$_3$ was prepared following a two-step procedure. A detailed description is provided elsewhere.$^3$ Briefly, MgSO$_4$ was mixed with Rutile (TiO$_2$) and treated at 800 °C in air. Obtained powders were converted to Mg:SrTiO$_3$ by mixing and grinding with SrCO$_3$ and calcination at 1100 °C for 10 h. The ratio of materials was adjusted to enable synthesis of Sr$_{1.25}$Mg$_{0.3}$TiO$_x$, hereafter identified by Mg:SrTiO$_3$. Detailed characterization (see also results section on HR-TEM/EDX and ICP analysis) shows that the
actual Mg content is lower in the active Mg:SrTiO$_3$ composite. This is caused by significant dissolution of Mg upon suspension in water, needed for washing, Ni impregnation, and photodeposition of CrO$_x$.

To deposit core/shell-type Ni/NiO co-catalysts, $0.2$ g Mg: SrTiO$_3$ or SrTiO$_3$ was dispersed in $20$ mL of an aqueous solution of Ni(NO$_3$)$_2$. The obtained mixture was stirred for $2$ h and afterwards the solution was evaporated till dryness ($80$ °C, overnight). The Ni-precursor was converted to NiO at $400$ °C ($10$ K min$^{-1}$ ramp rate) in synthetic air ($30$ mL min$^{-1}$), followed by treatment in $5\%$ H$_2$/N$_2$ ($80$ ml min$^{-1}$) at $500$ °C ($10$ K min$^{-1}$) for $10$ h. Core/shell Ni/NiO structures were obtained by cooling the tube furnace to $130$ °C in $5\%$ H$_2$/N$_2$ ($80$ ml min$^{-1}$), before introducing N$_2$ and subsequently air ($30$ ml min$^{-1}$) for $1$ h. The Ni loading was verified to be $1$ wt% by XRF analysis.

Modification with chromium oxide was achieved by photodeposition. Briefly, $0.1$ g of Ni/NiO-Mg: SrTiO$_3$ was dispersed in $10$ mL of a $10$ mM K$_2$Cr$_2$O$_4$ solution ($\mathrm{pH} \sim 5$). The resulting slurry was illuminated for $3$ hours using a UV LED light source ($365$ nm, $3.2$ mW cm$^{-2}$). Afterwards the obtained powder was separated from solution by filtration and dried at $80$ °C for $12$ h. The amount of CrO$_x$ was verified to be $0.2$ wt% in all cases by X-ray fluorescence (XRF) analysis.

Photocatalytic activity experiments

The photocatalytic activity of the synthesized photocatalysts ($25$ mg catalyst in $25$ mL DI water) was measured using a continuously stirred tank reactor ($30$ mL cuvette, 402.013-OG obtained from Hellma), equipped with a gas-tight lid. Products were stripped from the reactor with a continuous He flow of $10$ mL min$^{-1}$, unless otherwise specified, and analyzed using a gas chromatograph equipped with a highly sensitive Pulsed Discharge Detector (Interscience). Apparent quantum efficiencies were determined using $365$ nm LED illumination (Roithner LaserTechnik), with a measured intensity of $1.9$ mW cm$^{-2}$. The area of illumination was $2.25$ cm$^2$ for all experiments and oxygen was removed from the solution prior to illumination by He purge overnight.

Characterization

XRD measurements were performed with a Bruker D2 (Cu K$_\alpha$ source) Diffractometer. Raman spectroscopy was performed at room temperature using an Avantes AvaRaman spectrometer, equipped with a $785$ nm laser. A Philips PW 1480 analyzer was used for XRF analysis. XPS was measured using a Quantera SXM from Physical Electronics using monochromatic Al K$_\alpha$ radiation ($1486.6$ eV). All spectra were calibrated to the carbon C1s peak at $284.8$ eV. Detailed TEM analysis was performed at different magnifications. Survey imaging of the fresh Ni/NiO-Mg: SrTiO$_3$ and CrO$_x$-modified Ni/NiO-Mg: SrTiO$_3$ was performed using a JEOL 2010F microscope, operating at $200$-kV. Local elemental analysis was obtained from a probe-corrected JEOL ARM200F scanning TEM (STEM), operating at $200$ kV, equipped with a
windowless EDAX X-ray detector and a Gatan Enfinium EELS spectrometer. High resolution TEM (HRTEM) imaging at 300kV was performed with an aberration-corrected FEI Titan instrument.

*In situ* ICP-MS measurements were performed in a photoelectrochemical scanning flow cell (SFC) connected to an inductively coupled plasma mass spectrometer (ICP-MS) (NexION 300X, Perkin Elmer). Daily calibration was performed with a four-point calibration at concentrations of (0; 0.5; 1; 5) µg l⁻¹ for Mg, Ti, Ni, Cr and Sr with standard solutions (Merck Certipur) mixed in DI water (Merck Milipore). Sc(Mg, Ti), Co(Ni) and Y(Cr, Sr) solutions at 10 µg l⁻¹ in 1% HNO₃ were used as internal standards. Several photocatalysts (Ni/NiOₓ-SrTiO₃, Ni/NiOₓ-Mg:SrTiO₃ and CrOₓ-modified Ni/NiOₓ-Mg:SrTiO₃) were immobilized by drop casting from aqueous suspension on glassy carbon substrates. The loading of every individual measurement spot was ~15 µg and a spot size of around 1.2 mm was used (Figure 1). A flow of liquid DI water of 186 µL min⁻¹ was introduced, and the water composition was analyzed after contact with the sample. The flow was maintained for 10 minutes in darkness, after which the photocatalyst was exposed to light (385 nm, 60 mW cm⁻², Thorlabs M385F1) for 5 minutes. Finally, the water flow was maintained for an additional 15 minutes in the dark. The Sr, Ti, Mg, and Ni-contents in the effluent were analyzed by integration over the various treatment periods (light on/off). Additionally, ICP-OES analysis (*ex situ*) of liquid aliquots taken during activity measurements were performed using a Perkin Elmer 8300dv to determine concentrations of dissolved Cr, Mg, and Ni at different stages of the reaction. Prior to the ICP-OES analysis the photocatalyst was isolated from the slurry solution by filtration, and only isolated clear solutions were used for analysis.

**Results And Discussion**

**Performance evaluation: Overall water splitting and backreaction**

The photocatalytic water splitting activities induced by UV light illumination (365 nm LED light source) of Mg:SrTiO₃ with either Ni/NiOₓ or CrOₓ-modified Ni/NiOₓ co-catalysts are compared in Figure 2a.

The initially rapid increase in apparent gas production for both catalysts is due to the characteristic residence time of product gas in the reactor and feed-lines to the GC, and the time needed to reach steady state CSTR behavior. A decrease in gas production is observed for Ni/NiOₓ-Mg:SrTiO₃ under continuous operation, which we previously assigned to changes in oxidation state and morphology of the core/shell Ni/NiO particles in Ni/NiOₓ-SrTiO₃. Remarkably, after CrOₓ-modification the stability of the photocatalyst is significantly improved, retaining at least 90% of the steady state photocatalytic activity after 70 hours of day/night cyclic operation (5.6 µmol g⁻¹ min⁻¹ of H₂ is produced, see Figure S1). Considering the measured photon flux of the 365 nm LED light, the apparent quantum yield (AQY) is calculated to be 26±2% for CrOₓ-modified Ni/NiO-Mg:SrTiO₃ (for data on simulated solar illumination, see Figure S2).
Figure 2b shows the effect of the presence of Mg-doping on the beneficial effect of photodeposition of CrOx. Interestingly, CrOx modification of Ni/NiOx-Mg:SrTiO3 hardly leads to improvement (the H2 production yield obtained after 8 h only increases from 510 µmol·g⁻¹ to 550 µmol g⁻¹), while the steady state performance of Ni/NiOx-Mg:SrTiO3 was improved by a factor of ~2 by photodeposition of CrOx. In the absence of Mg, CrOx furthermore has a significantly smaller positive effect on the stability (Figure S3). These observations suggest that Mg is essential to achieve the positive effect of CrOx on the performance of Ni/NiOx core/shell particles.1,10

In studies on photocatalytic water splitting, significant improvements in activity and selectivity due to CrOx-modification are generally assigned to suppression of the unfavorable oxygen reduction reaction (ORR) by forming a protective shell around particularly Rh nanoparticles.25 Therefore we determined the photocatalytic performance of the Mg-doped composites in the presence of exogenous oxygen (and hydrogen). In the absence of light, neither Ni/NiOx-Mg:SrTiO3 nor the CrOx-modified Ni/NiOx-Mg:SrTiO3 photocatalyst induces (chemical) conversion of O2. Figure 3 compares the characteristic photocatalytic performance (rate is displayed on the left y-axis and the AQY on the right y-axis) of (CrOx-modified) Ni/NiOx-Mg:SrTiO3 when purging 80 ppm of H2 and 80 ppm of O2. Once initiating illumination, H2 and O2 are produced resembling the trends observed in pure He purge (compare Figure 2). Terminating illumination results in a fast transient in gas production, and concentrations quickly stabilize to the background levels. Re-initiating illumination recovers gas production, with Ni/NiOx-Mg:SrTiO3 continuing deactivation. Since the partial pressure of oxygen in continuous flow reactors is typically low in comparison to batch-type systems,26–28 the absence of the oxygen reduction reaction (at 80 ppm) was to be expected.10,29

This is further confirmed by a transient in feed gas from He to the gas containing 80 ppm of H2, O2 and N2 during photocatalytic experiment (Figure S4), hardly showing any effect of this gas compositional change on performance. Finally, production rates of H2 and O2 are independent of the purge-gas flow rate (Figure S5),26,28 which should not be the case if reduction of oxygen occurs.28,30,31 Summarizing, these results show that Ni/NiO core-shell structures appear to be poor catalysts for the ORR at the concentrations relevant for the present study, and it is thus unlikely that suppression of unwanted side reactions by CrOx deposition explains the enhanced performance of CrOx promoted NiOx-Mg:SrTiO3.10 Alternatively, we propose that a mixed oxide formulation of CrOx and Ni/NiOx (and Mg) is formed, which is highly effective in the water reduction reaction, and enhances the stability against dissolution of NiOx phases. First we will provide evidence for the formation of mixed Cr and Ni oxide phases, and will discuss the spatial distribution of CrOx in the composite, followed by a detailed study of dissolution of NiOx in the investigated catalytic formulations.
Materials Characterization: Localizing photodeposited CrO$_x$

In an attempt to localize CrO$_x$ on the surface of the prepared photocatalysts, XRD (Figure S6), Raman (Figure S7), XPS and (HR/S)TEM were used. XRD, Raman and XPS were not able to provide any evidence of the oxidation state, nor crystal structure of CrO$_x$ and as such CrO$_x$ appears to be present in low quantities on the surface.

The oxidation states of the Ni/NiO$_x$ co-catalyst on the surface of Ni/NiO$_x$-Mg: SrTiO$_3$ and CrO$_x$-modified Ni/NiO$_x$-Mg: SrTiO$_3$ were determined by XPS for both, as-prepared, and measured samples. In as-prepared Ni/NiO$_x$-Mg: SrTiO$_3$ (Figure S8a) the Ni 2p$_{3/2}$ signal mainly consists of contributions from Ni$^{2+}$ (NiO at 853.5 eV). A minor contribution of metallic Ni$^0$ (851.9 eV) is also revealed. After illumination, the width and symmetry of the Ni signal changed, which suggests that the relative contribution of Ni$^{2+}$ (as in Ni(OH)$_2$ at 855.6 eV) is significantly enhanced as compared to Ni$^0$. Formation of NiOOH might also contribute to the overall peak shape. This assignment is also in agreement with the changes in the O1s signal induced by illumination (Figure S9). In contrast, Ni and O signals of the CrO$_x$-modified Ni/NiO$_x$-Mg: SrTiO$_3$ composite show little difference, before and after illumination (Figure S8b), suggesting that NiO$_x$ preserves the oxidation state (Ni$^{2+}$ (as in Ni(OH)$_2$ at 855.6 eV) and presumably some NiOOH). In fact the dominant presence of oxidized Ni-species in the as-prepared CrO$_x$-modified Ni/NiO$_x$-Mg: SrTiO$_3$ is likely due to the applied photodeposition procedure, in which the most stable Ni oxidation state was formed.

TEM images showing the morphology of the as-prepared photocatalysts are compared in Figure 4a-d. All materials exhibit large Mg: SrTiO$_3$ particles in the order of 100s of nanometers. Ni/NiO$_x$ core shell particles decorate the surface throughout and are roughly 5-30 nm in size with a shell thickness of approximately 2 nm (for HRTEM images of Ni/NiO$_x$ particles the reader is referred to Figures S10-14). The morphology of the supported Ni/NiO$_x$ core-shell particles is rather heterogenous throughout each sample. Specifically, for some core-shell particles low contact angles (indicating good bonding to the support) are revealed, whereas weak interfaces with larger contact angles are observed for others.

To investigate differences in the structure of the Ni/NiO$_x$ particles on each photocatalyst composite in more detail, both before and after undergoing photocatalytic measurements, HRTEM imaging was performed. Figure 5a shows a typical core-shell particle as observed for CrO$_x$-modified Ni/NiO$_x$-Mg: SrTiO$_3$, being almost indistinguishable from particles analyzed in (Cr-free) Ni/NiO$_x$-Mg: SrTiO$_3$ (see for comparison Figures S12 and S14). In Figure 5b, the corresponding FFT is displayed showing the presence of Ni, NiO, and Ni(OH)$_2$, in agreement with XPS analysis and previous observations reported for
Ni/NiO<sub>x</sub>-SrTiO<sub>3</sub> composites after illumination. Thus, we suggest Ni(OH)<sub>2</sub> most likely forms as a result of illumination during photodeposition of CrO<sub>x</sub>. Using inverse FFT analysis (Figure S9), the distribution of the different phases was explored and shows a clear Ni core surrounded primarily by NiO and smaller patches of Ni(OH)<sub>2</sub> (see Figure 5c, additional images are shown in Figure S11 and S13). Interestingly, no CrO<sub>x</sub> overlayers were found surrounding any of the imaged Ni/NiO<sub>x</sub> particles on both the as-prepared and used CrO<sub>x</sub>-modified Ni/NiO<sub>x</sub>-Mg: SrTiO<sub>3</sub>. Nominally, there is no difference between the supported particles on either sample and particle growth that may result from the deposition of a CrO<sub>x</sub> layer is absent. Moreover, the Ni/NiO<sub>x</sub> particles are barely distinguishable from that on Ni/NiO<sub>x</sub>-Mg: SrTiO<sub>3</sub> (see Figures S12 and S14 for HRTEM images) suggesting the Cr incorporation is very subtle and may indeed be present in mixed oxide species.

To further examine the CrO<sub>x</sub>-modified Ni/NiO<sub>x</sub>-Mg: SrTiO<sub>3</sub> photocatalysts STEM was used and EDX and EELS (see supporting information Figure S15) spectra were collected from the surface and the bulk of the material. In total, fifteen regions over the surface containing Ni/NiO<sub>x</sub> particles, ten areas of the Mg: SrTiO<sub>3</sub> surface without supported particles, and seven entire aggregates (i.e., bulk) were inspected by EDX. Due to the low Cr signal (and Mg) in each individual EDX spectra, the different groups of spectra were summed and are displayed in Figure 4e. In all summed EDX spectra, the Cr signal is weak while the Ni signal is expectedly strong at regions of the surface containing Ni/NiO<sub>x</sub> particles. Considering that each spectrum contains a baseline Cr signal originating from constant objective lens pole piece excitation by X-rays emitted from the respective sample, Cr and Ni signals were normalized (for normalization procedure see supporting information). Figure 6 compares the integrated normalized Ni and Cr signals for EDX spectra collected from the bulk (Figure 6a), Ni/NiO<sub>x</sub> particles (Figure 6b), and the Mg: SrTiO<sub>3</sub> surface (Figure 6c). In addition, the Cr/Fe ratio (i.e., a ratio of the normalized Cr and Fe signals) for all spectra is shown in Figure S16. In all spectra collected from regions containing Ni/NiO<sub>x</sub> particles, the normalized Ni signal is about 3-40 times greater (left y-axis in Figure 6), than the average normalized Cr signal found in the bulk or at the bare Mg: SrTiO<sub>3</sub> surface (Figure 6, see also supporting information for additional information). Note that for clarity the baseline Cr signal attributed to the pole piece fluorescence, the mean and average error (7.22x10<sup>-2</sup> ± 2.37x10<sup>-2</sup>) of the integrated Cr signal associated with the bulk measurements is plotted (yellow areas) on all three graphs.

For about half of the regions possessing Ni/NiO<sub>x</sub> particles (i.e., spectra 2-3 and 11-15) also significant contributions of Cr were obtained. Interestingly, a very high Ni signal does not always correlate with a high Cr signal as revealed in spectra 8 and 11 (see Figure 6b and also Figure S17 comparing EDX data of spectra 8 and 15). Since roughly half (6 out of the 15 areas inspected with Ni/NiO<sub>x</sub> particles) contain additional Cr content beyond the background level, this implies that the photodeposition of CrO<sub>x</sub> onto Ni/NiO<sub>x</sub> has not been consistent for all particles. Finally, the low integrated Cr signal (Figure 6c) and Cr/Fe ratios (Figure S16) from regions of the Mg: SrTiO<sub>3</sub> surface are similar to that of the bulk, which further supports that CrO<sub>x</sub> was deposited preferentially onto several, likely specific Ni/NiO<sub>x</sub> particles, rather than uniformly throughout the surface. In contrast, the Mg peak is equal in all summed spectra indicating a
homogenous distribution of Mg throughout the bulk and surface of the support particles. The amount of Mg incorporated into the particles is consistent with a composition of $\text{Mg}_{0.03}\text{Sr}_{1.25}\text{TiO}_3$ according to EDX simulations done with NIST's DTSA-II software (Figure S18).

One can draw a few interesting and summarizing conclusions from the characterization and especially the EDX analysis. First, a dramatic effect in photocatalytic efficiency is observed, despite the small amount of Cr present and the absence of a continuous CrO$_x$ layer or coating. Likely a mixed-Ni-Cr oxide is formed on the nano-scale. Secondly, the heterogeneity of the Cr distribution and loading on the Ni/NiO$_x$ suggests that there are vast opportunities for further improvement of photocatalyst. Specifically, an increase in performance can be expected by achieving a more uniform distribution of CrO$_x$ in contact with the NiO$_x$/Ni particles. Two hypotheses can be proposed to explain the presence of CrOx in the vicinity of some, and the absence in the vicinity of others. First, the revealed heterogeneity in CrO$_x$ distribution may result from differences in the NiO$_x$ shell thickness. Very thick shells (which are probably insulating) may prevent photogenerated electrons to transfer from the Mg:doped SrTiO$_3$ semiconductor to the deposited Ni/NiO$_x$ particles, preventing reduction of Cr(VI)-ions in the photodeposition procedure. Conversely, any cracks within the NiO$_x$ shell would expose the Ni metal and promote photodeposition. The consistent shell thickness and continuity of the NiO shells in several images, however, does not strongly support this hypothesis. Another explanation for inhomogeneity, might be difference in the interfacial/electrical contact between the Ni/NiO particles and the Mg: SrTiO$_3$ support. Poor contact could also impede photodeposition from occurring. A similar effect has been observed on Ni/NiO core/shell structures on TiO$_2$ wherein the photocatalyst deactivates due to a photochemical reaction causing Ni to dissolve into solution.$^{20}$ In this case, only a fraction of the particles exhibited the Ni leaching which was believed to result from the good electrical contact between the light-absorbing TiO$_2$ support and Ni particles. Several supported particles on the Mg: SrTiO$_3$ supports studied here were characterized by low contact angles (see Figures S10-14), indicative of a strong interfacial contact that likely facilitates charge transport. As such it even seems likely that a poor electrical interfacial contact between the Ni particles and the perovskite support will not only limit the photodeposition of CrO$_x$ but will also limit the water splitting activity. In summary, improved catalyst preparation techniques aimed at establishing excellent contact between Ni/NiO$_x$ and (doped) SrTiO$_3$ phases, may result in further enhancement of the photocatalytic activity.

**Accessing Photocatalyst Stability**

We will now address the beneficial effect of CrO$_x$ on the stability of the catalyst. Sophisticated *in situ* ICP-MS analysis of dissolution of various elements is therefore required,$^{27,32}$ and was combined with *ex situ* analyses.$^{22,24}$ Three different photocatalysts were analyzed by in situ ICP-MS, namely Ni/NiO$_x$-SrTiO$_3$, Ni/NiO$_x$-Mg: SrTiO$_3$ and CrO$_x$-modified Ni/NiO$_x$-Mg: SrTiO$_3$, to understand the influence of Mg and CrO$_x$ in more detail. These are shown in Figure 7.
It is immediately evident that Sr leaches rapidly from all samples (Figure 7a). In fact rapid leaching occurs primarily upon contacting with water (Figure S19 and Figure S20). Interestingly, Sr dissolution is most significant for Ni/NiO<sub>x</sub>-Mg: SrTiO<sub>3</sub>, suggesting that the presence of Mg promotes formation of an unstable surface structure. After photodeposition of CrO<sub>x</sub> the quantity of Sr dissolution from Ni/NiO<sub>x</sub>-Mg: SrTiO<sub>3</sub> is reduced significantly. The fraction of Sr accumulated in 5 minutes of illumination at 385 nm is comparatively small (Figure 7b), and the relative amounts for the three investigated semiconductor composites are similar as compared to the total accumulated amount of dissolved Sr. Detected quantities of Cr, Ni, and Mg were comparatively low and no Ti was detected for all photocatalyst composites tested. Similarly to Sr dissolution, Mg leaching appeared to be reduced after photodeposition of CrO<sub>x</sub>. It is important to emphasize that initiating and terminating illumination did not result in significant transients in Sr dissolution or other elements.

In Figure 7c dissolution of Ni is summarized. Dissolution of Ni is rapid and predominant in the first 10 minutes of aqueous flow (dark). Interestingly, dissolution of Ni is significantly lower for Mg-containing photocatalysts as compared to Ni/NiO<sub>x</sub>-modified SrTiO<sub>3</sub> (stoichiometric), suggesting that Mg stabilizes the interaction of Ni/NiO<sub>x</sub> with the surface of the semiconductor, in agreement with the previously discussed electron microscopy data. The addition of CrO<sub>x</sub> appears to further enhance Ni stability against leaching, although it is important to emphasize that leaching of the most instable Ni particles might have also occurred during the CrO<sub>x</sub>-photodeposition procedure.

The results obtained by in situ ICP-MS regarding Ni dissolution are supported by ex situ ICP-OES analysis of the filtered solutions obtained at different times of activity testing (Figure 8). Though the overall amount of dissolved material is still low, again the largest quantities of dissolved Ni were determined for Ni/NiO<sub>x</sub>-SrTiO<sub>3</sub>. Interestingly, following Ni<sup>2+</sup> quantities in solution during testing of Ni/NiO<sub>x</sub>-Mg: SrTiO<sub>3</sub>, suggested that some Ni<sup>2+</sup> is redeposited/adsorbed in the absence of light.

During illumination the determined quantity of dissolved Ni is significantly lower compared to the initial phases of testing, i.e. reactor purging before illumination (Figure 8a, blue bars). For all CrO<sub>x</sub>-modified photocatalysts, leaching of Ni is clearly less pronounced and appeared to be constant already after 3 hours of exposure to the solution while purging (brown and yellow bars in Figure 8a). Ni leaching is even further suppressed for Mg-containing Mg: SrTiO<sub>3</sub> materials (yellow bars). Focusing on the Mg content in the solution, the presence of Ni/NiO<sub>x</sub> suppressed Mg dissolution (compare green and blue bars in Figure 8b). Addition of CrO<sub>x</sub> further suppresses Mg-leaching, which is otherwise most significant after illumination (after measurement).
Summarizing, *in situ* and *ex situ* ICP analysis show that: i) Sr leaching is significant for SrTiO$_3$ and even more so for Mg:SrTiO$_3$, ii) Mg is also found in solution, of which the quantity is smaller after photodeposition of CrO$_x$, iii) leaching of Ni is significantly reduced for Mg-containing SrTiO$_3$, and iv) photodeposition of CrO$_x$ further reduces leaching of Ni/NiO$_x$.

Considering these results and the provided TEM analysis, we propose that mixed metal-oxides are formed, i.e. containing Ni and Cr, likely anchored with low contact angles on surfaces terminated by Mg-containing crystal orientations. The establishment of such conformations, is likely a function of leaching phenomena occurring during photodeposition. Certainly, the implications of dissolution on the performance and stability of photocatalysts used for overall water splitting (or CO$_2$ reduction) in aqueous media are of great importance to guide material development and industrial applicability of photocatalysts.

**Conclusion**

This work demonstrates, using state of the art high resolution microscopy and (*in situ*) elemental ICP analysis to follow metal dissolution, that stability of complex heterogenous photocatalysts can be improved by additives, only present in traces. We have demonstrated that active co-catalyst phases of Cr and Ni are likely formed, preferably at locations with low contact angles between Ni/NiO core shell particles and the Mg:SrTiO$_3$ surface, allowing effective charge transfer during the photodeposition procedure of CrO$_x$. Stability metrics such as metal dissolution are proposed here to be implemented in ongoing research to find efficient and durable photocatalysts to drive overall water splitting.

**Declarations**

**ASSOCIATED CONTENT**

**Supporting Information.** Additional photocatalytic activity and stability data (Fig. S1-S4), Raman, XRD and XPS analysis (Fig. S5-S8), supporting HRTEM images (Figure S9-S13), STEM-EELS (Figure S14), and STEM-EDX (Figure S15-S17) results.

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Abbreviations

XRD, x-ray diffraction; XPS, x-ray photoelectron spectroscopy; TEM, transmission electron microscopy; EDX, energy-dispersive x-ray; ICP, inductively coupled plasma; MS, mass spectrometry; OES, optical emission spectrometry.

References

(1) Chiang, T. H.; Lyu, H.; Hisatomi, T.; Goto, Y.; Takata, T.; Katayama, M.; Minegishi, T.; Domen, K. Efficient Photocatalytic Water Splitting Using Al-Doped SrTiO$_3$ Coloaded with Molybdenum Oxide and Rhodium–Chromium Oxide. ACS Catal. 2018, 2782–2788. https://doi.org/10.1021/acscatal.7b04264.

(2) Lyu, H.; Hisatomi, T.; Goto, Y.; Yoshida, M.; Higashi, T.; Katayama, M.; Takata, T.; Minegishi, T.; Nishiyama, H.; Yamada, T.; Sakata, Y.; Asakura, K.; Domen, K. An Al-Doped SrTiO$_3$ Photocatalyst Maintaining Sunlight-Driven Overall Water Splitting Activity for over 1000 h of Constant Illumination. Chem. Sci. 2019, 10(11), 3196–3201. https://doi.org/10.1039/c8sc05757e.

(3) Han, K.; Lin, Y.-C.; Yang, C.-M.; Jong, R.; Mul, G.; Mei, B. Promoting Photocatalytic Overall Water Splitting by Controlled Magnesium Incorporation in SrTiO$_3$ Photocatalysts. ChemSusChem 2017, 10(22), 4510–4516. https://doi.org/10.1002/cssc.201701794.

(4) Zhao, Z.; Goncalves, R. V.; Barman, S. K.; Willard, E. J.; Byler, E.; Perry, R.; Wu, Z.; Huda, M. N.; Moulé, A. J.; Osterloh, F. E. Electronic Structure Basis for Enhanced Overall Water Splitting Photocatalysis with Aluminum Doped SrTiO$_3$ in Natural Sunlight. Energy Environ. Sci. 2019, 12(4), 1385–1395. https://doi.org/10.1039/C9EE00310J.
(5) Ham, Y.; Hisatomi, T.; Goto, Y.; Moriya, Y.; Sakata, Y.; Yamakata, A.; Kubota, J.; Domen, K. Flux-Mediated Doping of SrTiO$_3$ Photocatalysts for Efficient Overall Water Splitting. *J. Mater. Chem. A* **2016**, *5*(0), 1–5. https://doi.org/10.1039/C5TA04843E.

(6) Takata, T.; Jiang, J.; Sakata, Y.; Nakabayashi, M.; Shibata, N.; Nandal, V.; Seki, K.; Hisatomi, T.; Domen, K. Photocatalytic Water Splitting with a Quantum Efficiency of Almost Unity. *Nature* **2020**, *581*(7809), 411–414. https://doi.org/10.1038/s41586-020-2278-9.

(7) Goto, Y.; Hisatomi, T.; Wang, Q.; Higashi, T.; Ishikiriyama, K.; Maeda, T.; Sakata, Y.; Okunaka, S.; Tokudome, H.; Katayama, M.; Akiyama, S.; Nishiyama, H.; Inoue, Y.; Takewaki, T.; Setoyama, T.; Minegishi, T.; Takata, T.; Yamada, T.; Domen, K. A Particulate Photocatalyst Water-Splitting Panel for Large-Scale Solar Hydrogen Generation. *Joule* **2018**, *2*(3), 509–520. https://doi.org/10.1016/j.joule.2017.12.009.

(8) Chen, S.; Takata, T.; Domen, K. Particulate Photocatalysts for Overall Water Splitting. *Nat. Rev. Mater.* **2017**, *2*, 17050. https://doi.org/10.1038/natrevmats.2017.50.

(9) Busser, G. W.; Mei, B.; Pougin, A.; Strunk, J.; Gutkowski, R.; Schuhmann, W.; Willinger, M.-G.; Schlögl, R.; Muhler, M. Photodeposition of Copper and Chromia on Gallium Oxide: The Role of Co-Catalysts in Photocatalytic Water Splitting. *ChemSusChem* **2014**, *7*(4), 1030–1034. https://doi.org/10.1002/cssc.201301065.

(10) Busser, G. W.; Mei, B.; Weide, P.; Vesborg, P. C. K.; Stührenberg, K.; Bauer, M.; Huang, X.; Willinger, M.-G.; Chorkendorff, I.; Schlögl, R.; Muhler, M. Cocatalyst Designing: A Regenerable Molybdenum-Containing Ternary Cocatalyst System for Efficient Photocatalytic Water Splitting. *ACS Catal.* **2015**, *5*(9), 5530–5539. https://doi.org/10.1021/acscatal.5b01428.

(11) Hisatomi, T.; Domen, K. Reaction Systems for Solar Hydrogen Production via Water Splitting with Particulate Semiconductor Photocatalysts. *Nat. Catal.* **2019**. https://doi.org/10.1038/s41929-019-0242-6.

(12) Maeda, K.; Teramura, K.; Lu, D.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. Photocatalyst Releasing Hydrogen from Water. *Nature* **2006**, *440*(7082), 295–295. https://doi.org/10.1038/440295a.

(13) Maeda, K.; Teramura, K.; Lu, D.; Saito, N.; Inoue, Y.; Domen, K. Roles of Rh/Cr2O3 (Core/Shell) Nanoparticles Photodeposited on Visible-Light-Responsive (Ga1-XZnx)(N1-XOx) Solid Solutions in Photocatalytic Overall Water Splitting. *J. Phys. Chem. C* **2007**, *111*(20), 7554–7560. https://doi.org/10.1021/jp071056j.

(14) Kanazawa, T.; Maeda, K. Light-Induced Synthesis of Heterojunctioned Nanoparticles on a Semiconductor as Durable Cocatalysts for Hydrogen Evolution. *ACS Appl. Mater. Interfaces* **2016**, *8*(11), 7165–7172. https://doi.org/10.1021/acsami.6b00907.

(15) Kurashige, W.; Mori, Y.; Ozaki, S.; Kawachi, M.; Hossain, S.; Kawawaki, T.; Shearer, C. J.; Iwase, A.; Metha, G. F.; Yamazoe, S.; Kudo, A.; Negishi, Y. Activation of Water-Splitting Photocatalysts by Loading
with Ultrafine Rh–Cr Mixed-Oxide Cocatalyst Nanoparticles. *Angew. Chemie Int. Ed.* **2020**, *59* (18), 7076–7082. https://doi.org/10.1002/anie.201916681.

(16) Domen, K.; Kudo, A.; Onishi, T.; Kosugi, N.; Kuroda, H. Photocatalytic Decomposition of Water into H2 and O2 over NiO-SrTiO3 Powder. 1. Structure. *J. Phys. Chem.* **1986**, *90* (26), 292–295. https://doi.org/10.1021/j100274a018.

(17) Townsend, T. K.; Browning, N. D.; Osterloh, F. E. Nanoscale Strontium Titanate Photocatalysts for Overall Water Splitting. *ACS Nano* **2012**, *6* (8), 7420–7426. https://doi.org/10.1021/nn302647u.

(18) Townsend, T. K.; Browning, N. D.; Osterloh, F. E. Overall Photocatalytic Water Splitting with NiOx–SrTiO3 – a Revised Mechanism. *Energy Environ. Sci.* **2012**, *5* (11), 9543. https://doi.org/10.1039/c2ee22665k.

(19) Han, K.; Kreuger, T.; Mei, B.; Mul, G. Transient Behavior of Ni@NiO x Functionalized SrTiO 3 in Overall Water Splitting. *ACS Catal.* **2017**, *7* (3), 1610–1614. https://doi.org/10.1021/acscatal.6b03662.

(20) Zhang, L.; Liu, Q.; Aoki, T.; Crozier, P. A. Structural Evolution during Photocorrosion of Ni/NiO Core/Shell Cocatalyst on TiO 2. *J. Phys. Chem. C* **2015**, *119* (13), 7207–7214. https://doi.org/10.1021/jp512907g.

(21) Zoontjes, M. G. C.; Han, K.; Huijben, M.; van der Wiel, W. G.; Mul, G. The Effect of Rh Δ+ Dopant in SrTiO 3 on the Active Oxidation State of Co-Catalytic Pt Nanoparticles in Overall Water Splitting. *Catal. Sci. Technol.* **2016**, *6* (21), 7793–7799. https://doi.org/10.1039/C6CY01424K.

(22) Knöppel, J.; Zhang, S.; Speck, F. D.; Mayrhofer, K. J. J.; Schu, C.; Cherevko, S. Time-Resolved Analysis of Dissolution Phenomena in Photoelectrochemistry – A Case Study of WO3 Photocorrosion. *Electrochem. commun.* **2018**, *96*, 53–56. https://doi.org/10.1016/j.elecom.2018.09.008.

(23) Klemm, S. O.; Topalov, A. A.; Laska, C. A.; Mayrhofer, K. J. J. Coupling of a High Throughput Microelectrochemical Cell with Online Multielemental Trace Analysis by ICP-MS. *Electrochem. commun.* **2011**, *13* (12), 1533–1535. https://doi.org/10.1016/j.elecom.2011.10.017.

(24) Zhang, S.; Rohloff, M.; Kasian, O.; Mingers, A. M.; Mayrhofer, K. J. J.; Fischer, A.; Schu, C.; Cherevko, S. Dissolution of BiVO 4 Photoanodes Revealed by Time-Resolved Measurements under Photoelectrochemical Conditions. *J. Phys. Chem. C* **2019**, *123* (38), 23410–23418. https://doi.org/10.1021/acs.jpcc.9b07220.

(25) Maeda, K.; Teramura, K.; Lu, D.; Saito, N.; Inoue, Y.; Domen, K. Noble-Metal/Cr2O3 Core/Shell Nanoparticles as a Cocatalyst for Photocatalytic Overall Water Splitting. *Angew. Chemie - Int. Ed.* **2006**, *45* (46), 7806–7809. https://doi.org/10.1002/anie.200602473.
(26) Fabian, D. M.; Hu, S.; Singh, N.; Houle, F. a; Hisatomi, T.; Domen, K.; Osterloh, F. E.; Ardo, S. Particle Suspension Reactors and Materials for Solar-Driven Water Splitting. *Energy Environ. Sci.* **2015**, *8* (10), 2825–2850. https://doi.org/10.1039/C5EE01434D.

(27) Mei, B.; Han, K.; Mul, G. Driving Surface Redox Reactions in Heterogeneous Photocatalysis: The Active State of Illuminated Semiconductor-Supported Nanoparticles during Overall Water-Splitting. *ACS Catal.* **2018**, *8* (10), 9154–9164. https://doi.org/10.1021/acscatal.8b02215.

(28) Takanabe, K. Addressing Fundamental Experimental Aspects of Photocatalysis Studies. *J. Catal.* **2019**, *370*, 480–484. https://doi.org/10.1016/j.jcat.2018.10.006.

(29) Dionigi, F.; Vesborg, P. C. K.; Pedersen, T.; Hansen, O.; Dahl, S.; Xiong, A.; Maeda, K.; Domen, K.; Chorkendorff, I. Suppression of the Water Splitting Back Reaction on GaN:ZnO Photocatalysts Loaded with Core/Shell Cocatalysts, Investigated Using a $\mu$-Reactor. *J. Catal.* **2012**, *292*, 26–31. https://doi.org/10.1016/j.jcat.2012.03.021.

(30) Takanabe, K. Photocatalytic Water Splitting: Quantitative Approaches toward Photocatalyst by Design. *ACS Catal.* **2017**, *7* (11), 8006–8022. https://doi.org/10.1021/acscatal.7b02662.

(31) Qureshi, M.; Takanabe, K. Insights on Measuring and Reporting Heterogeneous Photocatalysis: Efficiency Definitions and Setup Examples. *Chem. Mater.* **2017**, *29* (1), 158–167. https://doi.org/10.1021/acs.chemmater.6b02907.

(32) Spanu, D.; Minguzzi, A.; Recchia, S.; Shahvardanfard, F.; Tomanec, O.; Zboril, R.; Schmuki, P.; Ghigna, P.; Altomare, M. An Operando X-Ray Absorption Spectroscopy Study of a NiCu–TiO$_2$ Photocatalyst for H$_2$ Evolution. *ACS Catal.* **2020**, *10* (15), 8293–8302. https://doi.org/10.1021/acscatal.0c01373.