Overall photocatalytic water splitting with NiO$_x$–SrTiO$_3$ – a revised mechanism

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Received 26th June 2012, Accepted 20th August 2012
DOI: 10.1039/c2ee22665k

NiO$_x$ (0 < $x$ < 1) modified SrTiO$_3$ (STO) is one of the best studied photocatalysts for overall water splitting under UV light. The established mechanism for this and many other NiO$_x$ containing catalysts assumes water oxidation to occur at the early transition metal oxide and water reduction at NiO$_x$. Here we show that NiO$_x$–STO is more likely a three component Ni–STO–NiO catalyst, in which STO absorbs the light, Ni reduces protons, and NiO oxidizes water. This interpretation is based on systematic H$_2$/O$_2$ evolution tests of appropriately varied catalyst compositions using oxidized, chemically and photochemically added nickel and NiO nanoparticle cocatalysts. Surface photovoltage (SPV) measurements reveal that Ni(0) serves as an electron trap (site for water reduction) and that NiO serves as a hole trap (site for water oxidation). Electrochemical measurements show that the overpotential for water oxidation correlates with the NiO content, whereas the water reduction overpotential depends on the Ni content. Photodeposition experiments with NiCl$_2$ and H$_2$PtCl$_6$ on NiO–STO show that electrons are available on the STO surface, not on the NiO particles. Based on photoelectrochemistry, both NiO and Ni particles suppress the Fermi level in STO, but the effect of this shift on catalytic activity is not clear. Overall, the results suggest a revised role of NiO in NiO$_x$–STO and in many other nickel-containing water splitting systems, including NiO$_x$–La : KTaO$_3$, and many layered perovskites.

Introduction

Splitting water into hydrogen and oxygen gas using suspended photocatalysts is generally considered the cheapest option for renewable hydrogen generation from sunlight. However, photocatalysts that are capable of simultaneously reducing and oxidizing water are very rare. Nickel oxide loaded strontium titanate (SrTiO$_3$, STO) is one of the few materials that can achieve the reaction in both pure water and aqueous NaOH solutions, without the need for expensive platinum group elements. Consequently, there has been interest in NiO$_x$–STO and STO-based photocatalysts and for over three decades. Under UV irradiation, NiO$_x$–STO has been shown to photolyze water into H$_2$ (up to 100 μmol g$^{-1}$ h$^{-1}$) and stoichiometric O$_2$. Until today the accepted mechanism for NiO$_x$–STO and for many related photocatalysts, including NiO$_x$–La : KTaO$_3$, NiO$_x$–K$_4$Nb$_6$O$_{17}$, and NiO$_x$–Rb$_2$Nb$_6$O$_{17}$.

Broader context

The water splitting reaction is generally regarded as the most promising method of converting solar energy into carbon free fuel. Among other catalysts, the reaction is promoted by NiO$_x$ (0 < $x$ < 1)-modified SrTiO$_3$. This catalyst is particularly interesting because it does not require any rare elements to achieve its function. The accepted mechanism for water splitting with NiO$_x$–SrTiO$_3$ assumes that photogenerated electrons are transmitted to the Ni/NiO nanoparticles, which serve as proton reduction sites, whereas water oxidation occurs on the surface of SrTiO$_3$. Here we demonstrate an alternative mechanism, in which the NiO particles function as a water oxidation co-catalyst and the Ni particles as water reduction co-catalyst. This new interpretation is based on data from surface voltage spectroscopy, photoelectrochemistry, photo-labeling and irradiation experiments. Thus, NiO$_x$–SrTiO$_3$ should be reformulated as a three-component catalyst Ni–SrTiO$_3$–NiO. The revised model resolves an old contradiction by Baba and Fujishima who stated in 1986 that ‘NiO on SrTiO$_3$ powders was not the cathodic site for hydrogen evolution’. The model also has implications for other NiO$_x$ containing photocatalysts, including NiO$_x$–La : KTaO$_3$, NiO$_x$–K$_4$Nb$_6$O$_{17}$ and NiO$_x$–Rb$_2$Nb$_6$O$_{17}$. 
and NiO$_x$–Rb$_2$Nb$_2$O$_7$, it assumes that NiO$_x$ functions as the proton reduction site, whereas water oxidation occurs at STO (or the layered metal oxide) using valence band holes. Based on high resolution electron microscopy data it has been shown that at least some of the NiO forms a shell around the Ni particles which might function as a barrier for the reduction of oxygen, in analogy to the Cr$_2$O$_3$ shell in a related Rh–Cr$_2$O$_3$ system.$^{31}$ This established mechanism further assumes that STO acts as a photoanode, which is consistent with the n-type character of STO. Here we present experimental data that suggest that NiO–STO should instead be regarded as a three-component photocatalyst with a Ni water reducing cocatalyst and a separate NiO water oxidizing cocatalyst. This interpretation is supported by irradiation tests on Ni–STO–NiO photocatalysts with systematically varied composition, which demonstrate that the three components, STO, Ni, and NiO, are required for function. Furthermore, data from surface photovoltage (SPV) spectroscopy show that electron trapping occurs on Ni and hole trapping on NiO, and photolabeling experiments with platinum confirm that in NiO–STO–NiO photocatalysts the photoelectrons are predominantly located at STO and not at NiO. Finally, the assignments of Ni as a cocatalyst for proton reduction and that of NiO as a cocatalyst for water oxidation agree well with measurements of the electrochemical overpotentials of the catalysts. The reformulation of NiO–STO as a three-component system Ni–STO–NiO sheds a new light on this important photocatalyst and suggests new ways for optimizing its performance.

**Results and discussion**

Scheme 1 gives an overview of the preparation of materials relevant to this study. SrTiO$_3$ (STO) was prepared from a high temperature solid state synthesis from precursors.$^{21}$ Nickel and NiO were coupled to the STO via three complementary methods. Either capped nickel nanoparticles were co-precipitated with STO followed by reductive annealing to produce Ni(add)–STO or STO was irradiated in a Ni$^{2+}$ solution to photodeposit nickel metal to generate Ni(hv)–STO. Or lastly, an aqueous solution of Ni(NO$_3$)$_2$ was deposited onto STO, followed by reductive annealing and re-oxidation at 130 °C to form R500–O130–NiO–STO and at 500 °C to form R500–O500–NiO–STO. In a subsequent step, the latter material was further modified by irradiating it in the presence of aqueous NiCl$_2$. This photo-deposits nickel metal to produce Ni(hv)–R500–O500–NiO–STO.

The crystal structure and phase purity of STO were verified with powder XRD (Fig. 1). TEM images (Fig. 2A) of STO showed a particle size range of 100 nm–1 µm. Based on TEM and STEM images, R500–O130 NiO–STO was covered with both nickel metal and nickel oxide (Fig. 2B and inset) as revealed by a combination of dark and lighter (high Z-contrast) sites. Photo-deposited NiO–STO showed small (4–6 nm) nickel particles distributed across STO (Fig. 2C and inset). In the case of Ni(add)–STO, 5–15 nm nickel nanoparticles can be seen to cover the surface of STO (Fig. 2D). Upon photodeposition of nickel onto R500–O500–NiO–STO, nickel particles (5–10 nm) are visible as dark contrast particles (5–10 nm) in addition to larger NiO particles (25–50 nm) from the initial oxidation process (Fig. 2E). Pt(hv)–R500–O500–NiO–STO (Fig. 2F) shows discrete photolabeled Pt particles (0.5–1.0 nm) on the STO surface in addition to separated NiO particles (5–10 nm). Similar to the Ni particles in Ni(hv)–NiO–STO, the Pt particles appear to be spatially isolated from the NiO sites.

UV/Vis diffuse reflectance spectra of unmodified STO (white powder, Fig. 3A) and NiO-activated STO catalysts (grey powders) show optical absorption onset between 3.0 and 3.2 eV, in agreement with the reported indirect band gap of 3.20 eV (O 2p → Ti 3d $t_2g$/$e_g$).$^{24}$

Only small changes occur upon addition of Ni nanoparticles, which is mostly a result of the low Ni content (3% mass) in the samples and the small Ni particle sizes (<5 nm in Ni(hv)–STO and <15 nm in Ni(add)–STO). In contrast, both R500–O25–Ni–STO and R500–O130–NiO–STO show a broad sub-band gap absorption with a peak at around 2.6 eV. Similar optical features have been previously attributed to SrTiO$_3$ doping with transition metal ions, including Ni$^{2+}$ and Fe$^{2+}$.$^{25,26}$

Surface photovoltage (SPV) spectroscopy is a useful tool for the characterization of photo-induced charge transfer processes in inorganic semiconductors and photocatalysts.$^{27–31}$ In SPV a light-induced change of the contact potential difference (∆CPD versus gold) of a sample is recorded as a function of the irradiation wavelength/energy. This produces positive or negative photovoltages, depending on the direction of charge transport. Spectra for thin films of STO and nickel derivatives are shown in Fig. 3B. Unmodified STO only produces a small ∆CPD signal of −70 mV, at photon energies of 3.4 eV, above the optical band gap of the material. The negative sign signifies that electrons are separated towards the gold substrate and that holes accumulate on the surface of the material. When the STO particles are coated with a NiO barrier, more significant positive ∆CPD signals are observed, indicating the presence of a NiO–STO–NiO three-component photocatalyst.

**Scheme 1** Synthesis of STO and NiO and Ni derivatives.

**Fig. 1** Powder X-ray diffraction pattern of synthesized STO.
with NiO as in R500−O130−NiO−STO, the negative ΔCPD signal increases and reaches a value of −460 mV at 3.68 eV. The enhancement of the positive polarization of the sample suggests that NiO serves as a hole-trapping material. In contrast, Ni(add)−STO yields a positive ΔCPD trace suggestive of electron trapping on the sample. The maximum value of this signal (+370 mV) is reached at 3.80 eV, at similar photon energy as in the preceding spectra. A positive ΔCPD signal is also observed for Ni(hn)−STO, but here the maximum ΔCPD value (+220 mV) is slightly smaller. Both of these materials predominantly contain Ni(0) and only a small fraction of NiO (from sporadic exposure to air at 25°C). Therefore, we conclude that Ni(0) acts as an electron trap on the STO. This interpretation agrees well with the concept of photochemical diodes where metal particles on photocatalysts act as electron acceptors and with the use of Ni(0) as a catalyst for the hydrogen evolution reaction.11,32–34

To specifically probe the effect of the NiO/Ni ratio in R500−O25 Ni−STO on charge separation, the compound was subjected to controlled oxidation by heating in air at 25 °C → 50 °C → 100 °C → 130 °C → 500 °C, followed by cooling to 25 °C. In this series, subsequent calcination steps convert an increasing amount of the nickel metal into NiO. The corresponding SPV spectra for the series are shown in Fig. 4A. While the first two samples yield positive SPV signals indicating electron trapping in the film, the latter samples show negative SPV spectra, with increasing size of the CPD value. This further confirms the interpretation of nickel metal particles acting as electron traps whereas NiO particles serve as hole traps. The proposed mechanism of charge separation in the three systems is also shown schematically in Fig. 4B.

When both Ni metal and NiO are present, the effects of electron and hole trapping compensate each other. This situation is most closely realized in the R500−O50 Ni−STO sample. The chemical transformation of Ni(0) into NiO is also reflected in the morphologies of the materials. While most of the cocatalyst particles in R500−O25 Ni−STO are pure nickel (based on contrast), some show evidence of a less dense shell that is presumably made of NiO (inset of Fig. 4C), as has been previously observed by Domen and coworkers.5 The more strongly oxidized sample R500−O130 NiO−STO shows a combination of high Z-contrast Ni particles and low Z-contrast NiO particles (Fig. 4D), and lastly, R500−O500 NiO−STO displays only large (50–100 nm) NiO particles of low contrast (Fig. 4E), in agreement with full Ni oxidation at the higher oxidation temperature.

In order to verify the proposed charge separation scheme in Fig. 4B, a photo-labelling experiment was performed with R500−O500−NiO−STO. The material was dispersed in pure water and irradiated in the presence of H2PtCl6 (no methanol was added to avoid reduction of NiO). Under these conditions Pt4+ gets quickly reduced to Pt(0) by photoelectrons generated in STO. A HRSTEM image of the irradiated material is shown in Fig. 5A. Small Pt particles (0.1−1 nm) can be found on the surface of the STO particles, clearly separated from the larger (5–10 nm) NiO particles (Fig. 2F). The identity of the particles is confirmed by repeated EDS line scans on the Ni (K,L) and Pt (L) emission lines (Fig. 5B). The fact that Pt(nv) is reductively photodeposited onto the STO surface and not onto the NiO particles supports the role of NiO as a hole acceptor in the NiO−STO system, as proposed in Fig. 4B.
In order to gain further insight into the roles of Ni and NiO, catalyst powders were dispersed in pure water under inert atmosphere and irradiated with a 300 W Xe arc lamp ($\lambda > 250$ nm). As the most active catalyst, R500–O130–NiOx–STO was found to evolve stoichiometric amounts of H$_2$ and O$_2$ over the entire 24 h time interval with the activity slightly diminishing after the first 5 h to a final 28 $\mu$mol g$^{-1}$ h$^{-1}$ (Fig. 6A). This activity is about 30% of the value for bulk NiO–SrTiO$_3$ (100 $\mu$mol g$^{-1}$ h$^{-1}$) reported by Domen in 1982. Slightly lower activity (22.5 $\mu$mol g$^{-1}$ h$^{-1}$, Fig. 6B) and sub-stoichiometric O$_2$ evolution were observed for Ni(hr)–STO, indicating that water oxidation was a limiting factor in this catalyst.

Interestingly, R500–O500–NiO–STO was not active at all (Fig. 6C), possibly owing to the lack of nickel metal in this material. To verify this hypothesis, nickel nanoparticles were photodeposited onto the inactive R500–O500–NiO–STO to obtain Ni(hr)–R500–O500–NiO–STO. This did activate the material for stoichiometric H$_2$O$_2$ evolution at a rate of 6.86 $\mu$mol g$^{-1}$ h$^{-1}$, as shown in Fig. 6C. Finally, Ni(add)–STO was also found to be active for stoichiometric H$_2$O$_2$ evolution, although at low rates (5.3 $\mu$mol g$^{-1}$ h$^{-1}$, Fig. 6D). In order to determine to what extent this catalyst was limited by the low content of NiO, the material was calcined in O$_2$ at 130 °C for 1 h. This treatment did increase the activity of the catalyst by 27% (Fig. 6D), signifying the importance of NiO in the catalysts. Overall, the irradiation experiments showed that the presence of both nickel metal and NiO is required for efficient stoichiometric H$_2$O$_2$ evolution.

To further probe the involvement of Ni and NiO in the water splitting process, electrochemical scans were conducted on films of the catalysts on gold electrodes immersed in phosphate-buff ered water at pH = 7. Potential current curves are shown in Fig. 7 and calculated overpotentials are listed in Table 1. Water reduction is found to occur at potentials negative of $-0.50$ V for all catalysts. Unmodified STO and pure NiO have the largest overpotentials for proton reduction ($\eta = 0.44$ V and 0.47 V, respectively). The attachment of Ni particles to STO reduces the overpotential to 0.39 V for Ni(hr)–STO and to 0.36 V for Ni(add)–STO. The catalyst containing both NiO and Ni (R500–O130 NiOx–STO) has $\eta = -0.35$ V, i.e. +0.09 V better than unmodified STO. This clearly shows that the Ni(0) metal promotes water reduction in these catalysts.

Anodic scans to probe the water oxidation potentials are shown in Fig. 7B. Water oxidation takes place at potentials between $+1.2$ V and $+1.6$ V, depending on the sample, and is accompanied by gas bubble formation at the electrode. Plain NiO ($\eta = 0.61$ V) was found to oxidize water most easily, followed by R500–O130 NiOx–STO ($\eta = 0.71$ V). Overpotentials for the remaining samples increase in order Ni(hr)–STO ($+0.77$ V) < Ni(add)–STO ($+0.78$ V) < STO ($+0.80$ V). As the latter samples contain the smallest fraction of NiO, the relative order shows clearly that the ease of electrochemical water oxidation is correlated with the NiO content in each catalyst. In
contrast, proton reduction is limited by the Ni metal content. These assignments also agree well with the literature. Nickel metal is widely known as an electrocatalyst for the HER reaction \(^{34-36}\) and NiO is an electrocatalyst for the oxygen evolution reaction (OER). \(^{37}\) The analysis also shows that \(h_{\text{OX}}\) values are about twice as large as the \(h_{\text{Red}}\) values. Thus the overall performance of the catalysts appears limited by the water oxidation kinetics. Indeed, it is well known that the best activity of NiO\(_x\)-STO can be achieved in alkaline solution, where water oxidation is thermodynamically more favorable. \(^{38}\)

Lastly, in order to observe the effect of Ni/NiO modification on the energetics of STO, photoelectrochemical scans were also performed on films of the catalysts on gold foil, immersed into 0.1 M aqueous KCl (pH 7) with 10% (vol) added methanol. The photo-onset potential \(E_{\text{Ph}}\) recorded under these conditions signifies the quasi Fermi level of the electrons in SrTiO\(_3\). \(^{39,40}\) For heavily n-doped materials, this value is close to the conduction

Table 1  Electrochemical and photoelectrochemical data. Water reduction and oxidation overpotentials (\(\eta\), at 0.90 mA cm\(^{-2}\)) are referenced against the thermodynamic potentials at pH 7 (\(-0.413 \text{ V NHE H}^+/\text{H}_2\) and +0.817 V NHE O\(_2/\text{H}_2\)O).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(E_{\text{Ph}}) (V VS. NHE)</th>
<th>(\eta_{\text{Red}}) (V)</th>
<th>(\eta_{\text{Ox}}) (V)</th>
<th>(H_2) rate ((\mu\text{mol g}^{-1} \text{h}^{-1}))</th>
</tr>
</thead>
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<tr>
<td>Bulk STO</td>
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<td>0.44</td>
<td>0.80</td>
<td>0.00</td>
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<tr>
<td>Ni((\text{add}))-STO</td>
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<td>0.36</td>
<td>0.78</td>
<td>5.33</td>
</tr>
<tr>
<td>Ni((\text{hv}))-STO</td>
<td>(-0.39)</td>
<td>0.39</td>
<td>0.77</td>
<td>22.5</td>
</tr>
<tr>
<td>R500-O130-NiO(_x)-STO</td>
<td>(-0.40)</td>
<td>0.35</td>
<td>0.71</td>
<td>28.0</td>
</tr>
</tbody>
</table>

Fig. 5  [A] HRSTEM image of Pt\((\text{hv})\)-R500-O500-NiO-STO and [B] EDS line scan.

Fig. 6  \(H_2\) and \(O_2\) evolution from 272 \(\mu\text{mol}\) (50 mg) NiO\(_x\) loaded STO suspended in 50 mL of water at pH 7 under full spectrum irradiation (>250 nm). [A] R500-O130-NiO\(_x\)-STO, [B] Ni\((\text{hv})\)-STO, [C] inactive R500-O500-NiO-STO (solid line) and activated Ni\((\text{hv})\)-R500-O500-NiO-STO (dashed line), [D] Ni\((\text{add})\)-STO-R500-O25 (solid line) and Ni\((\text{add})\)-STO-R500-O130 (dashed line).

Fig. 7  Photo-electrochemical water reduction [A] and oxidation [B] with NiO\(_x\)-STO films on the Au substrate, 10 mV s\(^{-1}\) scans, at pH = 7 in Na\(_2\)HPO\(_4\)-NaH\(_2\)PO\(_4\) buffer. All potentials are referenced against NHE.
band edge of the semiconductor. The electrochemical scans are shown in Fig. 8 and relevant data collected in Table 1. Observed photocurrents were 20 μA cm⁻² for STO but decreased to ~3 μA cm⁻² upon attachment of Ni/NiO. In the case of Ni(hv)-STO, photocurrents were too small to accurately determine the photono-onset. The photocurrent decrease is due to competitive light absorption by NiO and Ni particles in the UV region of the spectrum, increased electron hole recombination at the Ni–STO and STO–NiO interfaces and electron trapping at Ni particles.

For unmodified STO we obtain $E_{\text{Ph}} = -0.87 \text{ V}$, in excellent agreement with the pH-corrected value of $-0.89 \text{ V}$, NHE for the flatband potential of SrTiO₃ (Butler and Ginley, $-0.95 \text{ V}$ at pH 8.6). Upon attachment of NiO or Ni particles, the photo-onset potential shifts to values between $-0.67$ and $-0.41 \text{ V}$. Similar changes of $E_{\text{Ph}}$ were observed for niobate and titanate nanocrystals upon addition of platinum or IrOₓ nanoparticles. Because the Fermi energies of Ni, Pt, IrOₓ, and NiO are more positive than SrTiO₃, the electrochemical equilibrium causes electrons to move from SrTiO₃ to the cocatalyst.

The energetic of the photocatalysts are summarized in Fig. 9, in order of increasing photocatalytic activity (left to right). The SrTiO₃ conduction band edges were approximated with $E_{\text{Ph}}$ values from Table 1 (the true conduction band edges are at more negative potentials). The following trends can be observed in the diagram (in order of increasing activity). 1) The SrTiO₃ band edges become more positive. 2) The HER potential becomes more positive (proton reduction gets easier). 3) The OER potential becomes less positive (water oxidation gets easier).

Fig. 8 Photo-current scans of NiOₓ–STO films on the Au substrate, 10 mV s⁻¹ scan rate, at pH 7 in aqueous 0.1 M KCl containing 10 vol% methanol. Arrows mark values for $E_{\text{Ph}}$.

Conclusion

Overall, the findings presented here suggest that the Ni/NiO cocatalyst in the known NiOₓ–STO system may not just be involved in proton reduction but also in water oxidation. The interpretation of NiOₓ–STO as a three component system with a STO light absorber, a Ni proton reduction and a NiO water oxidation catalyst is supported by the following observations. 1) Both Ni metal and NiO are required as cocatalysts on SrTiO₃ for photocatalytic water splitting. 2) Non-active NiO–STO can be activated for water splitting by photodeposition of Ni metal. 3) Based on surface photovoltage spectroscopy, Ni acts as an electron trap and NiO as a hole trap. 4) Reductive photodeposition of Pt occurs on SrTiO₃, not on NiO, tracing photogenerated electrons in that material. 5) Based on electrochemistry, Ni(0) lowers the proton reduction overpotential, while NiO lowers the water oxidation overpotential. Additional photoelectrochemical data show that both Ni and NiO shift the photoonset potential (a measure of the SrTiO₃ conduction band edge) to more positive values, but it is not clear if this shift is significant for activity. The reinterpretation of NiO as the water oxidation site might be relevant to other NiOₓ–derived water splitting catalysts, including NiOₓ–La : K-TaO₃, NiOₓ–K₄Nb₄O₁₇, and NiOₓ–Rb₂Nb₂O₇. Similar to NiOₓ–STO, those catalysts also require partial re-oxidation of the Ni-component to reach optimal activity. The new findings also resolve an early contradiction by Baba and Fujishima in 1986, who conclude that ‘on the basis of the hydrogen separation factor analysis for NiO–SrTiO₃, it seemed that the surface of the deposited NiO on SrTiO₃ powders was not the cathodic site for hydrogen evolution’. Lastly, this work also shows that the performance of the Ni–STO–NiO system is limited by the electrochemical overpotential for water oxidation, which is twice as high as that for water reduction. Thus, an increase of the activity should be possible by replacing NiO with a more effective water oxidation catalyst. Or alternatively, alkaline conditions can be employed to promote water oxidation.
Experimental

Chemicals KOH 99.9%, oxalic acid 99.9%, Sr(NO₃)₂ 99.9%, P25 TiO₂, Ni(H₂O)₆(NO₃)₂ 99.9%, NiCl₂·6H₂O 99.9%, cetyltrimethylammonium bromide, CTAB, 99.9%, and n-hexanol 99.9% were purchased from Fisher Scientific, Pittsburgh, PA. Water was purified to 18 MΩ cm resistivity using a Nano-pure system.

STO particles

STO was synthesized via a high temperature solid state process³ where 0.02 mol, 1.74 g P25 TiO₂ was mixed and sonicated for 10 minutes with 0.026 mol, 5.53 g Sr(NO₃)₂ in a 1 : 1.2 molar ratio in 200 mL of water to produce precursors for 4 g of SrTiO₃. Aqueous oxalic acid (0.4 M, 1 : 1 molar ratio with Sr) was added drop wise to the solution under vigorous stirring. Conc. ammonium hydroxide was added slowly to increase the pH of the solution to 6.5 in order to precipitate strontium oxalate crystals onto the 25 nm TiO₂ particle surfaces via heterogeneous nucleation.⁴ When precipitation was complete, the white solid was centrifuged and washed 8 times in 50 mL of water, followed by drying in air at 100 °C. This precursor was calcined in a Thermolyne 79300 Tube Furnace to 1100 °C for 1 h with a heating rate of 10 °C min⁻¹. After cooling down to room temperature, the white solid was washed twice in 50 mL of 5 M HNO₃ to remove excess SrCO₃ followed by repeated water washes until the supernatant reached a pH of 7. Phase purity was confirmed by powder X-ray diffraction.

Modification with Ni(NO₃)₂

STO particles (200 mg, 1.10 mmol) were added to a 20 mL aqueous Ni(NO₃)₂·6H₂O solution (0.023 g, 3 wt% loading of NiO: STO), and the components were thoroughly mixed in a sonication bath for 10 min. This solution was dried at 100 °C and then annealed at 400 °C in air for 30 min to produce a grey colored solid. The solid was then heated in an H₂ atmosphere to 500 °C and maintained at that temperature for 1.5 h to remove nitrate as N₂(g) and H₂O(l) and to simultaneously reduce Ni²⁺ to Ni(0). After that, the black solid was heated in an O₂ atmosphere at 25 °C, 50 °C, 100 °C, 130 °C, or 500 °C for 30 min to induce oxidation of nickel to nickel oxide (NiOₓ, 0 < x < 1).⁵

Modification with nickel(i)

STO particles (50 mg, 2.7 × 10⁻⁴ mol) were suspended in 50 mL of aqueous methanol (1 : 1 v/v) containing 0.013 M (0.195 g) of NiCl₂·6H₂O. This mixture was irradiated using a xenon arc lamp for 24 h until the solution changed from white to dark grey.⁶ The resulting grey solid was centrifuged and washed 4 times with 50 mL of water followed by drying at room temperature.

Modification with nickel or platinum(ii)

Fully oxidized R500–O500–NiO–STO particles were prepared as described above by calcination at 500 °C. The solid was then dispersed in aqueous NiCl₂·6H₂O (0.013 M) solution and irradiated with a Xe arc lamp for 24 h. The product was obtained by centrifugation and washed four times in 50 mL of H₂O. No methanol was used in the preparation because irradiation in methanol can cause (back-) conversion of NiO to Ni. For the preparation of Pt(hv)–R500–O500–NiO–STO, H₂PtCl₆ (1.0 wt% Pt) was used in place of NiCl₂·6H₂O.

Modification with nickel(III)

Nickel nanoparticles (5–10 nm) were synthesized following a literature method.⁷ Two separate microemulsions (NiCl₂ [0.1 M]/CTAB/n-hexanol and Na₂H₄OH [3 M]/CTAB/n-hexanol, adjusted to pH 13 with conc. ammonia) were mixed giving a final wt% ratio = 22% H₂O : 33% CTAB : 45% n-hexanol. This solution was heated and stirred at 73 °C for 1 h to produce 5–10 nm Ni nanoparticles. STO particles (200 mg, 1.10 mmol) were added to 20 mL of this dispersion. The dispersion was mixed in a sonication bath for 10 min and the STO and Ni NPs were co-precipitated by adding 100 mL of methanol : chloroform (1 : 1 vol). The resulting solid was washed four times with 50 mL of H₂O and dried at 100 °C, in air. After an additional treatment in air (400 °C for 1 h) and H₂ (500 °C for 1 h), the sample was cooled down to 25 °C and handled in air.

Preparation of plain NiO

Ni(NO₃)₂·6H₂O was heated in air at 400 °C for 1 h, followed by H₂ atmosphere (500 °C for 1 h) and then O₂ (500 °C for 1 h) to form a dark green solid and phase verified with XRD (data not shown). Powder XRD scans were conducted with a Scintag XRD, at a wavelength of λ = 0.154 nm with 2 mm tube slit divergence, 4 mm scatter, 0.5 mm column scatter and 0.2 mm receiving widths.

Bright field high resolution transmission electron microscopy (HRTEM) and HR scanning transmission electron microscopy (HRSTEM) images were taken using a JEOL 2500SE 200 kV T/STEM. Energy Dispersive X-ray Spectroscopy (EDS) scans were taken in STEM mode with a ThermoNORAN Spectrophotometer and NORAN System SIX analysis program. Samples were prepared by immersing copper grids with a carbon film into aqueous dispersions of the samples followed by washing with water and air-drying.

UV/Vis diffuse reflectance spectra were recorded on dried powders on white Teflon tape using a Thermo Scientific Evolution 220 UV Vis spectrometer equipped with an integrating sphere.

For electrochemical measurements, thin films of the catalysts were prepared on a gold foil electrode (1.0 cm²) by drop coating and drying at 25 °C. A wire was attached to the bare gold back with conductive carbon tape and sealed with adhesive. The electrode was placed into a N₂-purged 3-electrode cell with a Pt counter electrode and a saturated calomel reference electrode connected to the cell with a KCl salt bridge. The cell was filled to 50 mL with 0.25 M Na₂HPO₄–NaH₂PO₄ buffer solution at pH 7, and the solution was degassed with N₂. Dark cyclic voltammetry scans were taken at 50 mV s⁻¹. The system was calibrated using the redox potential of K₄[Fe(CN)₆]₃⁻ at +0.358 V (NHE). For light measurements, 5 mL methanol was added to the solution, and chopped light was introduced into the cell using a fiber optics cable connected to a 300 W Xe arc lamp.

Surface photovoltage (SPV) measurements were conducted under vacuum (2 × 10⁻⁴ mBar) on SrTiO₃ films on gold.


