Hybrid photoanodes for visible light-driven water oxidation: the beneficial and detrimental effects of nickel oxide cocatalyst

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Abstract

Hybrid photoanodes comprising polymer-based light absorbers coupled to oxygen-evolving cocatalysts represent a promising, yes still underdeveloped, approach to photoelectrochemical splitting of water into hydrogen and oxygen. In this study, we investigate nickel oxide (NiO$_x$) nanoparticles as a water oxidation catalyst in hybrid photoanodes based on polymeric carbon nitride (CN$_x$) supported on electron-collecting mesoporous TiO$_2$ support. The performance of the resulting TiO$_2$–CN$_x$/NiO$_x$ photoanodes is evaluated with respect to our previous results on hybrid TiO$_2$–CN$_x$ photoanodes modified with IrO$_x$ and CoO(OH)$_x$ cocatalysts. The deposition of NiO$_x$ into TiO$_2$–CN$_x$ photoanodes enhances significantly the photocurrent (from $<8$ $\mu$A to $>250$ $\mu$A cm$^{-2}$ at 1.23 V vs. RHE) under visible light irradiation ($\lambda > 420$ nm, $\sim200$ mW cm$^{-2}$) and triggers the photoelectrocatalytic oxygen evolution. No oxygen evolution was observed without a cocatalyst. As compared to photoanodes modified with IrO$_x$ or CoO(OH)$_x$, the TiO$_2$–CN$_x$/NiO$_x$ photoanodes excel by the very negative photocurrent onset potential (0 V vs. RHE), which we ascribe to good hole-extracting properties of NiO$_x$. However, the comparatively low Faradaic efficiencies for oxygen evolution ($\sim18\%$) and dramatically decreased operational stability of the photoanodes indicate that the extracted holes do not efficiently oxidize water to dioxygen, but instead accumulate in the NiO$_x$ particles and increase thus the oxidative photodegradation of the photoanodes. Our study highlights the fact that employing outstanding electrocatalysts like NiO$_x$ in photoelectrochemical water-splitting systems does not necessarily lead to satisfactory results, especially when the photoelectrode cannot be operated at optimal pH due to light absorber stability issues.

1. Introduction

The ever-increasing energy demand worldwide is currently being supplied mostly by combustion of fossil fuels (coal, oil, gas), which is not sustainable in the long run and causes various environmental concerns. Therefore, there is an urgent need for an effective transition to renewable energy sources, such as solar energy [1, 2]. Apart from other technological concepts, solar-driven water splitting into molecular hydrogen and oxygen in photoelectrochemical (PEC) cells is considered a promising approach to directly convert and store solar energy in the form of chemical energy in ‘solar fuels’, i.e. either in hydrogen or in high-energy compounds, such as hydrocarbons or alcohols that can be obtained by reduction of CO$_2$ with hydrogen [3–6]. It should be noted that it is, in particular, the oxygen evolution reaction (OER) that, due to its inherent complexity, represents a major kinetic bottleneck of all water-splitting systems, and research on water oxidation catalysis has therefore attracted considerable attention over the last decades [7, 8]. Most investigated water-oxidizing photoanodes for PEC cells are based either on passivated high-quality
semiconductors (e.g. Si or III–V compounds) [9–11], or on low-cost metal oxides, such as Fe2O3 [12] or BiVO4 [13].

Apart from these rather conventional photoanode concepts, one of the promising—yet less explored—approaches is represented by so-called hybrid photoanodes that comprise a ‘soft’ molecular or polymeric photoabsorber supported on a wide-bandgap inorganic semiconductor or transparent conductive oxide, modified with an additional co-catalyst to promote the OER from water; for excellent reviews of recent developments in this field see Refs. [14–16]. One of the advantages of this concept is that the wide-gap semiconducting support (e.g. TiO2), acting as an electron collector, typically has a rather negative conduction band edge, which translates into relatively negative photocurrent onset potentials. This is, for example, beneficial in view of using such hybrid photoanodes coupled in tandem devices to photocathodes that do not have sufficiently positive photocurrent onset potential (e.g. silicon). An archetypal example of such architectures was reported by Mallouk et al who developed mesoporous TiO2 films sensitized by ruthenium(II) tris(bipyridine) dye and decorated with IrO2 nanoparticles as water oxidation catalyst [17, 18]. Apart from Ru-tris(bipyridine) complexes [19, 20], a whole range of other organic sensitizers based on perylenes [21–25], porphyrins [26, 27] and π-conjugated naphthalene benzimidazole polymers [28], typically coupled with IrO2 or CoOx cocatalyst, were investigated.

In our own research, we have investigated inorganic–organic hybrid photoanodes based on nanocrystalline TiO2 modified with an organic polymer, polymeric carbon nitride (‘CNx’), also called polyheptazine or, more precisely, poly(aminomino)heptazine or melon, a polymeric s-heptazine derivative, also referred to as ‘graphitic carbon nitride’ or ‘g-C3N4’ in the literature) [29], coupled with IrO2 or CoO(OH)2 co-catalysts [30–37]. The hybrid electrodes were prepared by depositing a thin layer of polymeric carbon nitride (CNx) onto mesoporous TiO2 scaffold on FTO glass using a chemical vapor deposition of urea pyrolysis products at 425 °C. Interestingly, the resulting TiO2–CNx hybrid’s optical absorption edge is extended into visible range as compared to unmodified TiO2 (3.2 eV) or CNx (2.9 eV) single components. We assigned the lower optical bandgap to a direct optical electron transfer from the HOMO of polymeric carbon nitride (CNx) to the conduction band edge of TiO2 due to strong electronic coupling between CNx and the TiO2 electron collector (figure 2(d)) [31]. Importantly, we found out that the TiO2–CNx photoanodes exhibit no dioxygen formation under visible light irradiation in the absence of a co-catalyst, even though anodic photocurrents were detected. In all our studies, dioxygen as a product of water oxidation was only observed after deposition of a proper cocatalyst [30–37]. This feature highlights the difference of hybrid photoanodes from more conventional photoanodes based on metal oxides, and establishes such hybrid photoanodes as a viable model system for investigations of the complex interplay between light absorbers and redox catalysts, the understanding of which is of utmost importance for the development of improved photo(electro)catalysts [38–41]. So far, our results indicated that the method of deposition, the size of co-catalyst particles, and the electrolyte composition were the key factors governing the overall photocactivity and stability of the TiO2–CNx photoanodes coupled with IrO2 or CoO(OH)2 cocatalysts [30–37]. In recent years, materials based on Ni oxide/hydroxide, always doped (either incidentally or intentionally) with Fe [42], have been established as outstanding OER electrocatalysts in basic media [42–51]. Inspired by the reports on excellent performance of NiOx electrocatalysts, herein we report on porous TiO2–CNx hybrid photoanodes loaded with NiOx catalyst for water oxidation under polychromatic visible light irradiation. Although the studied system underperforms in terms of photocactivity and stability as compared to our previously reported hybrid photoanodes coupled with IrO2 or CoO(OH)2, the NiOx co-catalyst is found to enhance charge extraction from the organic carbon nitride CNx layer and reveals cathodic shift of photocurrent onset potential for water oxidation. In addition, a comparative analysis of the performance of various cocatalysts in hybrid photoanodes is provided and discussed.

2. Experimental

2.1. Fabrication of TiO2–CNx photoanodes

The TiO2 electrodes as well as the TiO2–CNx hybrid photoelectrodes were prepared as we reported previously [31, 32, 37]. The FTO glass substrate with size of 1.5 × 2.5 cm was first cleaned by the 99.8% acetone solution (Merck, Germany) for removing residual organic contaminants by ultrasonication for 20 min. The cleaned FTO glass was then etched in 0.1 M sodium hydroxide and rinsed with deionized water. Firstly, the commercial TiO2 powder (0.5 g, Hombikat UV 100, Sachtleben, Germany, anatase, specific surface area (BET) ~300 m2 g−1, crystallite size <10 nm) was dispersed in ethanol solution (2.5 ml) by ultrasonication for 20 min. The resulting white suspension was applied on FTO coated glass using a doctor blade, followed by a hydraulic press under 200 kg cm−2 for 3 min and calcination at 450 °C for 30 min, as shown in the supporting information (figure S1(a) (available online at stacks.iop.org/JPENERGY/2/044001/mmedia)). This procedure results in ca. 4.1 ± 0.5 μm thick mesoporous TiO2 films on FTO.
Secondly, the deposition of polymeric carbon nitride (CN\textsubscript{x}) on the TiO\textsubscript{2} photoanode was achieved by chemical vapor deposition at 425 °C for 30 min using 1.0 g of urea (Merck) as the starting precursor, as shown in figure S1(b). For this, a glass reactor consisting of a Schlenk tube containing electrodes and connected to a round-bottom flask containing urea was placed into a muffle oven (Carbolite).
2.2. Deposition of NiO\(_x\) particles
The porous TiO\(_2\)–CN\(_x\) photoelectrodes were loaded with NiO\(_x\) particles using a two-step impregnation process (supporting information, figure S1(c)). First, the as prepared TiO\(_2\)–CN\(_x\) photoelectrodes were dipped into an aqueous solution of Ni(NO\(_3\))\(_2\) (1.0 M; Merck) for 10 min at room temperature and dried in air. Subsequently, the electrodes were dipped into an aqueous solution of NaOH (5.0 M) for 30 s and dried again in air. Dip-coating withdrawal speed for both steps were 100 mm min\(^{-1}\). The resulting photoanode is denoted as TiO\(_2\)–CN\(_x\)/NiO\(_x\). For comparison, NiO\(_x\) particles were also deposited onto TiO\(_2\) using the same procedure as described above, but without carbon nitride deposition (samples TiO\(_2\)–NiO\(_x\)). The above procedure was found optimal with respect to various factors—the optimal NiO\(_x\) loading (1, 2 or 3 dip coating cycles; figure S7), pH and concentration of the borate electrolyte (figure S6), and the dipping time in the hydroxide solution (not shown)—that resulted in the highest rate of oxygen evolution during photoelectrocatalysis.

2.3. Characterization methods
The optical properties of photoanodes were determined using a UV–vis diffuse reflectance spectroscopy (UV–Vis DRS; UV2600 spectrometer, Shimadzu) using FTO substrate as a reference; the absorbance \(Abs\) was calculated as \(1—R—T\), where \(R\) is the reflectance and \(T\) is the transmittance of the photoelectrode. The morphology and chemical composition of photoanode were investigated by scanning electron microscopy (SEM: Zeiss 1550, LEO), and energy dispersive x-ray spectroscopy (EDX), respectively. In order to estimate the iron content in NiO\(_x\), an excess of 5 M NaOH (3 ml) was added to 5.4 ml of Ni(NO\(_3\))\(_2\) (1.0 M) aqueous solution, the precipitate was washed with water, dried at 80 °C overnight, and the Fe content was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Horiba Jobin Yvon).

2.4. Photoelectrochemical measurements
The photoelectrochemical properties of the as-prepared hybrid photoanodes were measured using a SP-300 BioLogic potentiostat and standard three-electrode configuration consisting of a photoanode working electrode, a platinum wire counter electrode, and a Ag/AgCl (3.5 M KCl) reference electrode. Measurements of oxygen evolution and photocurrent onset were carried out under polychromatic irradiation by a 150 W of Xenon lamp (L.O.T.-Oriel) with intensity of around 200 mW cm\(^{-2}\) equipped with a KG3 heat-absorbing filter (LOT-Quantum Design) and a cut-off filter for visible light (\(\lambda > 420\) nm). The borate/boric acid electrolyte (0.1 M, AppliChem, Germany) of different pH values was used. The geometric area of working electrode was 0.5 cm\(^2\). The electrodes were irradiated from the backside (through the FTO glass). The evolved oxygen was monitored in a two-compartment cell by measuring the concentration of oxygen in the electrolyte using an OxySense 325i oxygen analyzer. The volume of the photoanode compartment was 4.6 ml. The oxygen values are not corrected for the losses in the gaseous headspace (2.4 ml); the collection efficiency of evolved oxygen in our two-compartment cell was approximately 75%, as estimated using direct electrolysis with a Pt working electrode. The baseline for oxygen evolution was corrected for a leakage by subtraction of the hydroxide solution (not shown)—that resulted in the highest rate of oxygen evolution during photoelectrocatalysis.

2.5. Electrocatalytic measurements
The oxygen values are not corrected for the losses in the gaseous headspace (2.4 ml); the collection efficiency of evolved oxygen in our two-compartment cell was approximately 75%, as estimated using direct electrolysis with a Pt working electrode. The baseline for oxygen evolution was corrected for a leakage by subtraction of the hydroxide solution (not shown)—that resulted in the highest rate of oxygen evolution during photoelectrocatalysis.

3. Results and discussion
3.1. Physical and optical properties
Nickel oxide/hydroxide (NiO\(_x\)) particles were deposited into the porous structure of TiO\(_2\)–CN\(_x\) hybrid electrodes by impregnation. The electrode was first soaked with nickel(II) nitrate aqueous solution (1.0 M) followed by drying and precipitation of NiO\(_x\) particles with sodium hydroxide (5.0 M) (figures S1 and 2(a)). It should be noted that NiO\(_x\) synthesized under such conditions typically contains small amount of ubiquitous iron impurities, making it thus catalytically active for OER [42]. The Fe content in our NiO\(_x\) was...
ca. 0.00075 wt%, as estimated by ICP-AES analysis of a larger amount (200.4 mg) of NiOx precipitate prepared from our reagents. Our efforts to add intentionally more iron during synthesis did not result in better photoelectrocatalytic performance (see below). The morphology of the TiO$_2$–CN$_x$/NiO$_x$ film was studied by scanning electron microscopy (SEM). The EDX elemental mapping (probe depth of ca. 1–3 µm) shows a rather inhomogeneous Ni distribution in the TiO$_2$–CN$_x$ photoanodes (figure 1). Some sampling areas showed very low concentration of Ni (~0.25 at.%), whereas other revealed much higher concentrations (~3.49 at%; supporting information, figure S2). Apart from nickel, the EDX elemental mapping confirmed, as expected, the presence of carbon, nitrogen, titanium and oxygen (figure S2); a small signals of silicon and sodium probably origin from the underlying FTO glass, whereas sodium could also arise from NaOH treatment during the deposition of NiO$_x$. Furthermore, the size distribution of the amorphous NiO$_x$ particles was very inhomogeneous, ranging from presumably small clusters (not visible in the SEM) to large particles with a size up to ~5 µm). The larger particles are two or three magnitudes bigger than IrO$_2$ and CoO(OH)$_x$ nanoparticles of size ~30 nm and 1–2 nm, respectively, employed in TiO$_2$–CN$_x$ electrodes in our previous studies [30, 37].

The absorbance spectra and Tauc plots of TiO$_2$, TiO$_2$–CN$_x$, TiO$_2$–NiO$_x$, and TiO$_2$–CN$_x$/NiO$_x$ electrodes are presented in figure 2(b) (see also figure S3). The spectra clearly show a shift of the absorption edge towards the visible for TiO$_2$–CN$_x$ (~2.5 eV) as compared to CN$_x$ (~2.9 eV) or TiO$_2$ (~3.2 eV) components (figure 2(c)). It should be noted that the optical absorption edge of the TiO$_2$–CN$_x$ hybrid (~2.5 eV) is slightly larger than the value we typically obtained in previous studies (~2.3 eV). This is possibly due to the inherent limitations of using the Tauc formalism for the bandgap determination of hybrid and composite materials [52], and due to the different estimation methods used; herein we measured directly the absorbance of photoelectrode films, whereas in the previous studies the diffuse reflectance spectra of corresponding powders were used for the determination of the absorption edge. More importantly, the UV–vis electronic absorption spectrum for TiO$_2$–CN$_x$/NiO$_x$ electrode is very similar to the spectrum of TiO$_2$–CN$_x$ without cocatalyst, indicating that the undesired optical absorption by NiO$_x$ particles is very low.

As a next step, we estimated the amount of electrochemically active Ni sites in the porous photoelectrodes by calculating the overall charge passed during the cathodic scan in cyclic voltammogram of TiO$_2$–CN$_x$/NiO$_x$ electrode in the dark (figure 3(a); for comparison see also for voltammograms without cocatalyst in supporting information, figure S4). We note that this estimation is rather comparative as we can presumably detect the redox response only of those catalyst particles that are in direct contact with the FTO substrate. At any rate, the total charge passed was ca. 0.29 mC cm$^{-2}$, a much lower value as compared to the value of 26.4 mC cm$^{-2}$ obtained for our previously investigated photoanodes modified with CoO(OH)$_x$ cocatalyst using an identical method [37]. The number of electrochemically active catalytic sites in NiO$_x$ cocatalyst is therefore much lower as compared to the CoO(OH)$_x$, which can be ascribed to the larger average size and inhomogeneous distribution of NiO$_x$ particles as compared to the CoO(OH)$_x$.

### 3.2. Photoelectrochemical properties of TiO$_2$–CN$_x$/NiO$_x$ photoanodes

The red shift of the optical absorption edge of TiO$_2$–CN$_x$ hybrids (figure 2(b)) and the very minor parasitic absorption of the cocatalyst enabled us to investigate the photoelectrocatalytic activity in water oxidation under polychromatic visible light using a longpass cut-off filter ($\lambda > 420$ nm), so as to effectively exclude the possible photoresponse from the TiO$_2$ support (absorption edge at 3.2 eV, corresponding to ca. 390 nm). First, we examined photocurrent response of the TiO$_2$–CN$_x$/NiO$_x$ electrode by potential-dependent photocurrent transient measurements under intermittent polychromatic visible light irradiation ($\lambda > 420$ nm) in a 0.1 M borate electrolyte in neutral pH. The photocurrent density of the TiO$_2$–CN$_x$/NiO$_x$ showed the highest value of >250 µA cm$^{-2}$ at 1.23 V vs. RHE. This value is much larger than the very low photocurrents of <8 µA cm$^{-2}$ at 1.23 V vs. RHE for control photoelectrodes based either on pristine TiO$_2$ that do not absorb in the visible ($\lambda > 420$ nm) or on TiO$_2$–CN$_x$ without a cocatalyst (figure 3(b)). The presence of the NiO$_x$ cocatalyst coupled to the TiO$_2$–CN$_x$ hybrid is therefore indispensable for the drastic photocurrent enhancement. Evidently, the NiO$_x$ cocatalyst enhances the extraction of the photogenerated holes from the carbon nitride layer and suppresses thus the charge recombination. Notably, though the fill-factor of the I–V curve is rather poor, the photocurrent onset potential for TiO$_2$–CN$_x$/NiO$_x$ of ~0.0 V vs. RHE (figure 3(b)) is very close to the conduction band edge of the electron-collecting TiO$_2$ ($E_{CB} = −0.15$ vs. RHE [53, 54]). This confirms that the photogenerated electrons are collected at the mesoporous TiO$_2$ scaffold, and their quasi-Fermi level is potentially negative enough to reduce protons to hydrogen, as we observed when TiO$_2$–CN$_x$ powders were coupled to hydrogenase as a hydrogen evolution catalyst and irradiated by visible light ($\lambda > 455$ nm) in the presence of EDTA as a sacrificial reducing agent [55]. It should be noted that the positive photocurrents near the onset potential are overlaid by dark negative current, which might be possibly overcome by employing of a proper blocking layer [56].
Figure 3. (a) Cyclic voltammogram of TiO$_2$–CN$_x$/NiO$_x$ recorded in the dark in 0.1 M borate solution (pH 7.0) at 5 mV s$^{-1}$; (b) photocurrents recorded under intermittent visible light irradiation ($\lambda$ > 420 nm) during cathodic potential sweep (5 mV s$^{-1}$).

Figure 4. (a) Photoaction spectra (incident photon-to-current efficiencies, IPCE) under intermittent (5 s light, 5 s dark) monochromatic irradiation measured at 1.12 V vs. RHE in borate solution (0.1 M; pH 7.0); (b) photocurrent transients and (c) oxygen evolution under polychromatic visible light irradiation ($\lambda$ > 420 nm) measured at 1.12 V vs. RHE of 0.1 M borate solution (pH 7.0).

The external quantum efficiencies of the photoanodes were recorded as wavelength-resolved Incident Photon-to-Current Efficiencies (IPCE) in neutral borate electrolyte (figure 4(a) and corresponding wavelength resolved photocurrent spectra in supporting information, figure S5). The photoaction spectrum onset at ca. 500 nm correlates well with the optical bandgap of ca. 2.5 eV for TiO$_2$–CN$_x$/NiO$_x$ composite. The IPCE values are increased by a factor of four at 420 nm upon coupling of the TiO$_2$–CN$_x$ photoanode with NiO$_x$ particles. It is worth noting that in case of the TiO$_2$–CN$_x$ photoanodes modified with IrO$_x$ nanoparticles that we investigated previously [30], the IPCE values were enhanced only by a factor of two. In this context, it is important to realize that, in the absence of the cocatalyst, the photocurrents can be essentially ascribed to oxidative photocorrosion of the TiO$_2$–CN$_x$ hybrid, especially of its carbon nitride component [30, 31, 37]. The here observed unusually low photocurrents for TiO$_2$–CN$_x$ without a cocatalyst can be interpreted in terms of diminished photocorrosion, possibly due to the beneficial effect of borate electrolyte on the photoelectrode stability as compared to phosphate and sulfate electrolytes we used in previous studies [30]. We note that the use of a borate electrolyte at pH 7, that is out of its optimal buffering range (pH 9.2), is substantiated by the fact that the photocorrosion of our TiO$_2$–CN$_x$ hybrids is significantly enhanced at higher pH values [30]. The deposition of NiO$_x$ cocatalyst allows for better hole extraction and opens the catalytic pathway for water oxidation to dioxygen (see below), which leads to a significant enhancement of photocurrents. This is also in line with results from prolonged (1 h) photocurrent measurements that also show the highest photocurrent for TiO$_2$–CN$_x$/NiO$_x$ during visible light driven ($\lambda$ > 420 nm) irradiation (figure 4(b)).

It is important to emphasize that, as in our previous results [30–37], the TiO$_2$–CN$_x$ photoanodes in the absence of the cocatalyst were not active in the OER under visible light ($\lambda$ > 420 nm). The visible light-driven dioxygen evolution occurs only after NiO$_x$ cocatalyst is deposited onto TiO$_2$–CN$_x$ electrode (figure 4(c)).
Figure 5. Stability test of different photoanodes: (a) photocurrent transients and (b) oxygen evolution recorded at photoanodes at 1.12 V vs. RHE in borate electrolyte (0.1 M; pH 7.0) under visible light irradiation ($\lambda > 420$ nm).

Figure 6. Comparison of the performance of TiO$_2$–CN$_x$ hybrid photoanodes modified with various cocatalysts: IrO$_x$ nanoparticles (average size ~30 nm) [30], ultrasmall CoO(OH)$_x$ nanoparticles (average size ~1–2 nm) [37], and NiO$_x$ nanoparticles [this work]: photocurrent density at different times after switching off the light; Faradaic efficiency (FE) of oxygen evolution measured after 1 h of irradiation under visible light ($\lambda > 420$ nm) irradiation; photocurrent onset potential vs. RHE during a cathodic potential scan.

Notably, the oxygen evolution could still be detected at an applied bias potential as low as 0.40 V vs. RHE (figure S8), which outperforms the so far best value of 0.56 V which we obtained at TiO$_2$–PH photoanodes modified with ultrasmall (~1–2 nm) CoO(OH)$_x$ nanoparticles [37]. Our results clearly indicate that NiO$_x$ cocatalyst particles trigger the dioxygen evolution from water, and also enhance the extraction of the photogenerated holes from the absorber, as evidenced by the relatively negative onset potential for oxygen evolution.

The long-term stability of the TiO$_2$–CN$_x$/NiO$_x$ photoanodes towards dioxygen evolution was tested by prolonged (3 h) visible light irradiation (figure 5). The TiO$_2$–CN$_x$/NiO$_x$ photoanodes showed poor stability, the photocurrent decreased significantly over time. Clearly, the TiO$_2$–CN$_x$/NiO$_x$ photoanodes suffer from severe degradation, most likely caused by the photocorrosion of the organic CN$_x$ layer, as the photoanode color becomes lighter after very long irradiation. The photocurrent decreased by about 55% already after 1 h of visible light irradiation, whereas for IrO$_x$ and CoO(OH)$_x$ cocatalysts [30, 37] the photocurrents remained relatively stable under similar experimental conditions (figure 6). Two further points are noteworthy. Firstly, the Faradaic efficiency (FE) of oxygen formation for TiO$_2$–CN$_x$/NiO$_x$ photoanode was very low (~18%),
which is ca. 2.4 times lower as compared to the FE values found for our photoanodes modified with IrO$_2$ (44%) and CoO(OH)$_x$ (42%) cocatalysts (figure 6) [30, 37]. Secondly, the presence of NiO$_x$ seems to accelerate the photocorrosion of the CN$_x$ layer, as the decrease of photocurrent is much more drastic than in case of a TiO$_2$–CN$_x$ without NiO$_x$. These results therefore suggest that the beneficial effect of NiO$_x$ in our hybrid photoanodes consists mainly in more effective hole extraction, leading to enhanced charge separation. However, the enhanced charge separation and accordingly higher photocurrents do not, unfortunately, translate into higher rate of oxygen evolution. In contrary, it is likely that most of the photogenerated holes that escape recombination due to effective extraction by NiO$_x$ contribute to more intense oxidative degradation of the hybrid photoelectrode, rather than to the desired oxygen evolution reaction. In other words, the NiO$_x$ cocatalyst particles not only extract the photogenerated holes, but also effectively store them, whereby they are positively charged. A similar behavior has been observed for Si photoanodes modified by NiO$_x$ passive layers [57]. This excess positive charge at NiO$_x$ particles induces only to a lesser part water oxidation to dioxygen, but mainly contributes to oxidative degradation of the carbon nitride layer or of the bond between the carbon nitride and TiO$_2$, resulting in poor performance stability and lesser reproducibility. It is likely that the sub-optimal oxygen evolving activity of our NiO$_x$ particles is related to the fact that our photoelectrodes are operated—due to photoanode stability issues—at neutral pH, whereas NiO$_x$-based catalysts typically require basic pH (ca. 13) for optimum performance. In case of TiO$_2$–CN$_x$/NiO$_x$ electrodes, the pH 7 turned out to be optimal (see supporting information, figure S6); higher pH affects negatively the stability of the polymeric carbon nitride [30, 37], while acidic conditions are detrimental to the stability and activity of NiO$_x$. In this context, we also point out that we have performed several further attempts, all without much success, to overcome the hampered kinetics for OER. Firstly, we tried to optimize the loading conditions of the NiO$_x$ particles. However, an increase of the loading of NiO$_x$ into TiO$_2$–CN$_x$ photoanodes by repeating the dip-coating cycles led to increased photocorrosion rate and diminished photoactivity (supporting information, figure S7). This was probably due to increased parasitic light absorption of the larger sized NiO$_x$ particles, as apparent from the electrodes becoming greenish to the naked eye. In order to optimize the photoanodes for higher oxygen evolution, we also tried to optimize the treatment with NaOH or ammonia of different concentrations (including zero concentration) and dipping times during NiO$_x$ deposition (data not shown).

Furthermore, in an effort to increase the OER activity of the NiO$_x$ cocatalyst, iron was intentionally added into the cocatalysts by dipping of the TiO$_2$–CN$_x$/NiO$_x$ electrode into Fe(NO$_3$)$_3$ solution (0.05 M or 0.1 M) followed by hydroxide treatment or by dipping of the TiO$_2$–CN$_x$ into a mixture of 1.0 M Ni(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ (0.05 M or 0.1 M) solutions. However, both approaches resulted in lower photoactivity toward the OER as compared to the TiO$_2$–CN$_x$/NiO$_x$.

4. Conclusion

In summary, we impregnated porous hybrid TiO$_2$–CN$_x$ photoanodes with NiO$_x$ cocatalyst and investigated their performance in visible ($\lambda > 420$ nm) light-driven water oxidation in borate electrolytes at neutral pH. In particular, we evaluated the photoelectrocatalytic properties of NiO$_x$-modified photoanodes with respects to our previously reported TiO$_2$–CN$_x$ photoanodes modified with IrO$_x$ [30] or CoO(OH)$_x$ nanoparticles [37]. In line with our previous studies, we observed triggering of photoelectrocatalytic oxygen evolution in the presence of the NiO$_x$ cocatalyst, whereby no oxygen evolution was observed without a cocatalyst.

However, the overall performance of the TiO$_2$–CN$_x$/NiO$_x$ photoelectrodes was worse than that of hybrid TiO$_2$–CN$_x$ photoanodes modified with IrO$_x$ or CoO(OH)$_x$, in particular in terms of the activity, long-term stability, and the Faradaic efficiency for oxygen evolution. For a useful comparative analysis of key figures of merit see figure 6. The only parameter in which the NiO$_x$-modified photoanodes outperform their counterparts is the very negative photocurrent onset potential of 0 V vs. RHE. We ascribe this beneficial effect of NiO$_x$ particles to more effective hole extraction from the TiO$_2$–PH light absorber. However, the very low Faradaic efficiencies for oxygen evolution and dramatically decreased stability of the photoanode performance indicate that the extracted holes are not efficiently oxidizing water to dioxygen, but instead accumulate in the NiO$_x$ particles and increase thus the oxidative photodegradation of our photoanodes. A possible future strategy to mitigate these negative effects might consist in combining NiO$_x$ nanoparticles that excel by very good hole extracting properties with cocatalysts like IrO$_x$ or CoO(OH)$_x$ that do not suffer so severely from oxygen evolving activity losses when they are operated at neutral pH. We also cannot rule out that some improvements can be achieved if alternative methods of NiO$_x$ deposition are employed, as the deposition procedure can influence the structural and catalytic properties of catalysts significantly [30, 37].

More generally, our study confirms the very complex interplay of various factors governing the behavior of NiO$_x$ catalysts when coupled to light absorbers. For example, Messinger and Liang studied BiVO$_4$ photoanodes modified with NiO$_x$ cocatalyst and they identified at least three different roles of NiO$_x$ at
BiVO$_4$, possibly related to different surface species, acting either as the oxygen evolution catalytic centers, the recombination centers, or the surface passivation centers [58]. In our case, the beneficial effect of NiO$_x$ related to its excellent hole extraction properties is unfortunately not matched by corresponding activity in catalysis of oxygen evolution. Our study thus highlights the fact that employing outstanding electrocatalysts like NiO$_x$ in photoelectrochemical water-splitting systems does not necessarily lead to satisfactory results, in particular when the photoelectrode cannot be operated at optimal pH (basic for NiO$_x$) due to the light absorber stability issues. Furthermore, the rather poor performance of our hybrid photoanodes as compared to the best conventional photoanodes based on metal oxides (photocurrents higher by the factor of ~10) and passivated silicon wafers (photocurrents higher by the factor of ~100, yet typically at higher bias potentials) raises also some uncomfortable questions about the very applicability of this type of photoanodes for solar water splitting. On one hand, it is surely true that these and similar ‘soft’ architectures can possibly compete with conventional photoanodes, let alone with combinations of photovoltaics with electrolyzers [59], only if truly disruptive breakthrough developments for significantly improved activity and stability during photoelectrocatalytic water oxidation are achieved. On the other hand, we believe that the scientific knowledge gained in studies of such complex systems comprising various combinations of light absorbers and cocatalysts might, in future, find application also in research fields beyond the solar water splitting, such as in light-driven selective organic synthesis and conversions of low value feedstock to high-value chemical compounds [60–62].

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of interest

The authors declare no conflict of interests.

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