DYE-SENSITIZED PHOTOCATHODES: MATERIALS AND INTERFACIAL PHOTODYNAMICS

Kaijian Zhu
DYE-SENSITIZED PHOTOCATHODES: MATERIALS AND INTERFACIAL PHOTODYNAMICS

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Kaijian Zhu

...born on the 25th of January, 1993
in Jiangsu, China
This dissertation has been approved by:

Supervisors:

prof. dr. G. Mul

dr. ir. J.M. Huijser

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Graduation Committee:

Chair / secretary: prof. dr. J.L. Herek

Supervisors: prof. dr. G. Mul
Universiteit Twente, TNW, Photocatalytic Synthesis

dr.ir. J.M. Huijser
Universiteit Twente, TNW, Photocatalytic Synthesis

Committee Members: prof.dr.ir. J. Huskens
Universiteit Twente, TNW, Molecular Nanofabrication

prof.dr.ir. H.L. Offerhaus
Universiteit Twente, TNW, Optical Sciences

prof.dr.ir. J.E. ten Elshof
Universiteit Twente, TNW, Inorganic Materials Science

prof. dr. J.N.H. Reek
Universiteit van Amsterdam

prof. dr. ir. R. van de Krol
Helmholtz-Zentrum Berlin für Materialien und Energie
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CHAPTER 1

Introduction
1.1 Solar energy

The world’s prosperity and economy have relied on exploiting fossil fuels such as oil, coal and gas since the industrial revolution. These rapid societal developments have resulted in a decline in natural resources and massive CO$_2$ emissions. As shown in Figure 1.1, based on the current consumption rate our fossil fuels can be expected to be depleted this century. In order to address resource and environmental issues, it is necessary to redesign the current energy infrastructure and develop renewable alternatives.

![Figure 1.1. Years of fossil fuels reserves left and CO$_2$ emission by fuel type.](image)

Sunlight is an abundant powerful energy source that is free, almost unlimited, and does not contribute to CO$_2$ emissions. Two common ways to use solar energy in daily life are photovoltaics and solar thermal technology. However, a variety of factors, including latitude, diurnal and seasonal changes, affect the amount of solar energy that reaches the Earth, resulting in intermittent availability of solar energy. Exploring how to directly convert and store solar energy is therefore of great interest. As inspired by Nature, artificial photosynthesis is a highly attractive and powerful approach for capturing and storing solar energy into chemical bonds, enabling storage and transport. Since Honda’s and Fujishima's pioneering discovery was published in 1972, research on artificial photosynthesis has substantially increased, especially during the last 20 years. Beyond TiO$_2$, which can only absorb ultraviolet light, materials including inorganic semiconductors, organic molecules, and polymers that can absorb visible light and even infrared light are now employed for artificial photosynthesis. Some large-scale prototypes such as 100 m$^3$ photocatalytic sheets for H$_2$ production (Figure 1.2a) and outdoor floating perovskite-BiVO$_4$ devices for proton or CO$_2$ reduction (Figure 1.2b) have demonstrated the potential of solar fuel technologies in the near future.
There are many ways to convert and store solar energy. The PV+electrolyzer, photoelectrochemical (PEC) cell, and photocatalyst powder system shown in Figure 1.3 are the three main techniques. Each of them has particular advantages and disadvantages. The powder system is the least expensive, but it is also the least efficient and needs additional gas separation equipment. The PV+electrolyzer combination can reach a high solar conversion efficiency, but with relatively high costs. In principle, the PEC cell sits in the middle, offering greater efficiency than the powder system while being less expensive than the PV+electrolyzer combination.

Theoretically, a tandem PEC cell with a photocathode and a photoanode can achieve a solar conversion efficiency >25%. There are many different types of photoelectrodes available now due to the developments in materials science, including traditional inorganic semiconductor electrodes like TiO$_2$, BiVO$_4$, Cu$_2$O, dye or quantum dot sensitized electrodes, organic polymer semiconductor electrodes, bio-photoelectrodes, etc. These PEC cells are based on a similar fundamental principle, which has been extensively reviewed in the literature. The dye-sensitized PEC cell will be the main focus of this thesis.
1.2 Dye-Sensitized Photoelectrochemical (DSPEC) cell

The first discovery of the photovoltaic effect was in 1839 by Becquerel, when a photocurrent was observed for two illuminated electrodes covered in silver halide and submerged in an electrolyte.\(^{19}\) Although the concept of an organic dye-sensitized semiconductor was initially proposed in the 1960s,\(^ {20}\) it was not until 1991 that O’Regan and Grätzel developed a solar cell based on dye-sensitized nanocrystalline TiO\(_2\) with a conversion efficiency up to 12\% in diffuse day light that it started attracting considerable attention.\(^ {21}\) Since then, the development of dye-sensitized solar cells (DSSCs) has accelerated. The first extension of such a dye-sensitized electrode from DSSC into a DSPEC cell was realized by Meyer in 1999, who used a TiO\(_2\) electrode functionalized with a chromophore-catalyst assembly.\(^ {22}\) The first application of such a DSPEC for water splitting was reported for a ruthenium tris(bipyridyl)-sensitized TiO\(_2\) photoanode in 2009,\(^ {23}\) and for a P1-sensitized NiO photocathode in 2012.\(^ {24}\) The Incident Photon to Current Efficiency (IPCE) with a 12.7 µA cm\(^{-2}\) photocurrent was around 0.9% under 450 nm light irradiation for the first dye-sensitized TiO\(_2\) photoanode for water oxidation, and has reached 29% with a photocurrent density of ~2.2 mA cm\(^{-2}\) after a decade of research.\(^ {25}\) On the other hand, the development of photocathodes normally based on dye-sensitized NiO is relatively slow.\(^ {8}\)

1.2.1 Working principle of DSPEC electrodes

![Figure 1.4](image)

**Figure 1.4.** (a) Design concept of the dye-sensitized photocathode: consisting of a nanocrystalline p-type semiconductor, light absorbing dye and catalyst. (b) Schematic representation of the three possible configurations generally employed to combine a dye with a catalyst.\(^ {26}\) TCO = Transparent Conducting Electrode.
A dye-sensitized photoelectrode used in solar fuel generation has a structure that is derived from a DSSC. As shown in Figure 1.4a, the organic chromophore is linked to a nanocrystalline semiconductor (n-type for photoanodes and p-type for photocathodes) through e.g. carboxylic acid, phosphonic acid or siloxane anchoring groups. The structure of the anchoring group influences the photoinduced charge transfer processes (Figure 1.4a) and chemical stability. In contrast to the DSSC, an additional catalyst is required in order to regenerate the dye and drive the chemical reactions. As shown in Figure 1.4b, the catalyst can be 1) homogeneously dissolved in the electrolyte, 2) co-adsorbed on the semiconductor surface or 3) assembled with the dye through chemical bonding or another intermolecular interaction.

![Figure 1.5. Schematic diagram of a single photocathode DSPEC device.](image)

A series of steps need to take place to drive a chemical reaction. In a photocathode (Figure 1.5) the following reactions should occur:

1) Light absorption to promote the dye molecules (D) to the excited state (D*).  
2) Charge separation by hole transfer from the photoexcited dye D* into the valence band of the semiconductor, resulting in a dye D•- radical anion.  
3) Hole diffusion to the conducting substrate (Fluorine-doped Tin Oxide, FTO in this case) and the external circuit to reach the counter electrode.  
4) Electron transfer from D•- to the catalyst.  
5) Electron accumulation and the chemical reduction reaction, e.g. H₂ evolution or CO₂ reduction.  

Similar processes in a reverse direction should occur in a photoanode.

To drive the reaction in a single DSPEC device, a wide band gap is required. For example, solar water splitting requires the light absorber to have a bandgap of at least 1.23 eV to span the electrochemical potential of water oxidation and reduction. Taking energy losses due to the different interface junctions and kinetic overpotential into consideration, 1.6-2.4 eV is normally needed for effectively
driving solar water splitting. Furthermore, an external bias is always needed for a single DSPEC device. In order to fully utilize the solar spectrum and enable the chemical reaction without external bias, a p-n tandem device consisting of a p-type photocathode and a n-type photoanode in series has been proposed. Some examples are shown in Figure 1.6.

**Figure 1.6.** (a) Side- and top-views of a tandem PEC water-splitting device; (b, c) Examples of p-n tandem DSPEC cells.

As shown in Figure 1.6a, to optimally utilize solar energy, it is necessary for photocathode and photoanode to have different light absorption spectra, e.g. short wavelength light is absorbed by the front part of the device and long wavelength light by the back side. Mozer et. al. reported unbiased solar water splitting using a tandem cell with a BiVO₄ photoanode and a dye-sensitized NiO photocathode. Sun et. al. demonstrated the first tandem DSPEC device by using RuP-sensitized TiO₂ and RuP-sensitized NiO as the photoanode and photocathode (Figure 1.6b). The combination with a Ru-based oxygen evolution catalyst and Co-based proton reduction catalyst successfully drove the water splitting reaction without external bias, with a steady photocurrent density around 25 μA cm⁻². By developing different dyes and catalysts (TiO₂/Lo/Ru1 and NiO/P1/Co1), they improved the photocurrent to ~70 μA cm⁻² with an internal photon to current efficiency (IPCE) of 25% at 380 nm. However, the efficiency of such a tandem device is much lower than of a single photoanode due to the low efficiency of the photocathode. There is one example where the photocathode outperforms the photoanode counterpart. Meyer et.al demonstrated a tandem cell with a perylene-diiimide derivative dye sensitized TiO₂-protected p-Si nanowire arrays cathode instead of NiO and a SnO₂[TiO₂]₂RuP₂²⁺RuCl₃ photoanode. The initial photocurrent for the tandem cell is around 300 μA cm⁻² and drops by ~31% after 2 h operation. The H₂ production quantum yield is around 0.32% over a 2 h period of...
irradiation. This work illustrates the importance to find a suitable photocathode material, and the lack of suitable photocathode materials currently hampers the development of efficient photocathodes and thus tandem DSPEC cells.

1.3 Photocathodes

As mentioned earlier, three crucial elements, a p-type semiconductor, a light absorber dye and a catalyst are typically needed in a photocathode to realize a chemical reaction. Substantial efforts have been made to develop efficient dyes and catalysts.\textsuperscript{26, 37}

1.3.1 Dye

The characteristics of a dye molecule are crucial for the DSPEC. A high extinction coefficient is required to allow a thin semiconductor layer with sufficient light absorption. This can lead to a reduction in the required hole transport distance and thus less charge recombination. For solar fuel applications, the HOMO level should be more positive than the top of the valence band of the p-type semiconductor to have sufficient driving force for photoinduced hole injection. Furthermore, the LUMO should be more negative than the redox potential of the electrolyte such as $E^\circ$ (H$^+$/H$_2$O), so the electron has sufficient electrochemical potential for the chemical reaction.

A variety of chromophores with several metal centers,\textsuperscript{38-39} different structures and number of anchoring groups 40 and various dye-catalyst assemblies\textsuperscript{41-42} have been explored to increase the stability, charge transfer rates and promote charge separation.\textsuperscript{37} Among these efforts, the design of the “push-pull” dye is an important step towards reducing charge recombination between the dye and the semiconductor. The “push-pull” structure contains a donor and an acceptor moiety, linked by a π-conjugated bridge. In a DSPEC photocathode, the donor site of the dye should be close to the semiconductor and the acceptor site point to the electrolyte. In this way, the electron is pushed away after photoexcitation, increasing spatial charge separation (Figure 1.7a). Furthermore, the length of the π-conjugated bridge can be tuned to further reduce charge recombination.\textsuperscript{43} So far, a variety of donor-π-acceptor (D-π-A) dyes have been designed, such as the benchmark dye P1 with a triphenylamine moiety as the electron donor and a malononitrile moiety as the electron acceptor.\textsuperscript{24, 44} Mozer reported perylenemonoimide (PMI, electron acceptor)- regioregular 3-hexyl substituted sexithiophene (6T bridge)- triphenylamine (TPA, electron donor) sensitized NiO to show long-term stability and H$_2$ evolution without additional catalyst.\textsuperscript{36} The BH4 dye with a single donor and two acceptors gives a high short-circuit current.\textsuperscript{45} The modification of the BH4 dye with additional hydrophobic tails allows it to work in extremely acidic conditions with good stability and photocurrent.\textsuperscript{46}

An important feature of the donor-acceptor dye that has not attracted much attention yet in DSPEC is the molecular twisting following photoexcitation. Figure 1.7b shows the Jablonski diagram of a donor-acceptor (D-A) system. In polar environments and in absence of major steric hindrance, the excited D-
A molecule undergoes fast intramolecular electron transfer from the locally excited (LE) state into the twisted intramolecular charge transfer (TICT) state, producing a relaxed twisted structure. This process results in a different fluorescence spectrum, a high energy band from the LE state and a lower energy band due to the emission from the TICT state. TICT is a non-radiative process, quenching the fluorescence of the LE state. Therefore, modification of the TICT process enables the design of functional molecules for various applications. However, whether the TICT state formed is beneficial or harmful for the functionality of a D-π-A dye in the photocathode is unknown.

Figure 1.7. (a) Chemical structure and HOMO and LUMO of a donor–acceptor dye, (b) Energy diagram of Twisted Intramolecular Charge Transfer (TICT) following light absorption of a D-A dye. GS = ground state of the original structure, LE = locally excited state, GS' = ground state of the twisted structure.

1.3.2 Catalyst

The catalyst is an important component in the DSPEC cell. It must be stable and have sufficient reduction potential after multi-step reduction for the H₂ evolution or CO₂ reduction reaction. Molecular catalysts are commonly used in DSPEC cells due to their high tunability and activity. Both electron transfer (ET) and proton transfer (PT) steps are essential for H₂ evolution of CO₂ reduction, with proton coupled electron transfer (PCET) favored over stepwise ET and PT due to the lower energy barrier. Therefore, it is important for the DSPEC performance to develop a catalyst that can undergo a PCET process.

In an initial attempt, the photocurrent was boosted about 5-fold by drop-casting the Co(dmgBF₂)₂(H₂O)₂ H₂ evolution catalyst onto P1-sensitized NiO. However, this drop-casting method is not suitable for long-term operation due to the poor mechanical stability and light-induced charge transfer properties. Therefore, later designs have focused on chromophore-catalyst assemblies, which can substantially increase the stability and charge transfer rate. Artero reported the first
covalently bound and noble-metal free dye-cobalt diimine–dioxime catalyst assembly on NiO for H₂ evolution in mildly acidic aqueous conditions. Meyer and colleagues realized a [Ru(dvb)₂bpy]²⁺ and [Re(dvb)(CO)₃Cl] (Re¹) catalyst for stable CO₂ reduction over 10 h with 65% Faradaic efficiency to CO. Wu designed a dirhodium complex that served both as sensitizer and catalyst to minimize losses due to intermolecular charge transfer from the dye into the catalyst. Kerlidou reported a covalent assembly of a ruthenium-based dye and a Co diamine dioxime catalyst, enabling to realize a photocathode with a high photocurrent density of 84 ± 7 μA·cm⁻².

1.3.3 p-type semiconductor NiO

NiO is the main p-type material employed in the dye-sensitized photocathode during the last two decades. NiO is a face-centered cubic structure material with a wide indirect band gap ranging from 3.4 to 4.3 eV. The wide band gap, suitable valence band position (~5.0 eV vs vacuum), optical transmittance and chemical stability cause NiO to be the commonly studied p-type semiconductor for DSPEC cells.

Stoichiometric NiO is an insulator with a room temperature conductivity of <10⁻¹³ Ω⁻¹cm⁻¹. However, NiO exhibits p-type conductivity due to the presence of Ni³⁺, which are formed due to the presence of Ni vacancies. The nature of the O 2p derived valence band of NiO leads to hole localization and a poor hole mobility. E.g. Li-doping also gives more Ni³⁺ defects, which allows to tune the conductivity. Though the Ni³⁺ defects can increase the conductivity, it is also problematic for NiO used in DSPEC cells. The Ni³⁺ defects are thought to give a gray-black color to NiO, which competes with the dye for light absorption. Furthermore, according to many studies the trap states induced by Ni³⁺ defects are likely the reason for the fast charge recombination between NiO and dye (or catalyst/electrolyte). Hammarström reported biphasic recombination kinetics in dye-sensitized NiO: a fast pathway with the holes in the NiO valence band and a slow pathway with the holes in trap states. A hole can be trapped at a surface Ni³⁺ site on a sub-picosecond time scale, much faster than by Ni²⁺ states typically occurring in a nanosecond time window. Tian and Cahoon found that passivation of Ni³⁺, Ni⁴⁺ and other defects in NiO could improve the DSSC performance. As the interface charge recombination between NiO and dye, catalyst or electrolyte is likely the limiting factor for DSPEC and DSSC, it is critical to develop fundamental insight into processes occurring at the NiO surface. The perfect NiO surface is suggested to be rather inert, but due to the existence of defects and dangling bonds the surface is complicated in reality. McKay found that pre-adsorbed O₂ on the NiO (100) surface plays an important role in dissociative adsorption of H₂O. O₂ is first adsorbed on a NiO (100) defect site, forming O²⁻. H₂O interacts with the adsorbed O²⁻ through a hydrogen bond, causing dissociation and forming OH⁻ bound to Ni ions. Surface coverage of OH⁻ on the NiO surface could decrease the work function. Freund also studied OH⁻ on NiO (100) and NiO (111) facets, and observed that hydroxylation on NiO (100) only happens at defect sites, but on NiO
(111) also at regular surface sites. Additionally, the resistivity of NiO was reported to change with time in a natural environment, with moisture in the air likely promoting surface deformation, highlighting the sensitivity of NiO to $\text{H}_2\text{O}$.

### 1.3.4 Other p-type semiconductors

P-type semiconductor like delafossite materials CuMO$_2$ (M= B, Al, Ga, Cr…) have been reported to have the potential to replace NiO. Different from the strongly localized valence band edge due to the O 2p orbitals in most metal oxides, hybridization of Cu 3d and O 2p orbitals causes delocalization of holes in the valence band. As a result, CuMO$_2$ shows a good hole mobility ($10^2$ – $10^2$ cm$^2$ V$^{-1}$ s$^{-1}$). Furthermore, weak direct interaction between Cu$^+$ ions and 3d$^{10}$ electrons gives a large band gap and high optical transparency. Tian compared the band gap and hole mobility of several p-type semiconductors, as shown in Figure 1.8. The large band gap, deep valence band position and high hole mobility make the p-type CuMO$_2$ materials promising to replace NiO in DSPEC cells.

Ishitani and Artero both reported that using CuGaO$_2$ instead of NiO in a DSPEC cell for CO$_2$ reduction or water splitting gives a 4 times higher photocurrent and 400 mV more positive onset potential. Reisner observed that the same dye and catalyst sensitized CuCrO$_2$ shows a higher photocurrent, Faradaic efficiency and turnover number than the NiO based analogue. Jobic investigated CuBO$_2$ as an alternative for NiO in a DSSC, but due to the presence of CuO impurities and large particles the overall efficiency is lower, despite the 150 mV higher open circuit voltage.

![Figure 1.8](image)

**Figure 1.8.** (a) Energy diagram for various p-type metal-oxide semiconductors; (b) Average transmission of visible light and hole mobility of several p-type metal oxides.
1.4 Bridging the time gap between charge separation and catalysis

Figure 1.9. Timescales of different processes in the DSPEC cell.

Photoinduced hole injection from a dye into NiO usually occurs in a time range of hundreds of femtoseconds to a couple of picoseconds and is followed by charge recombination in picoseconds to nanoseconds. However, the catalytic reaction occurs relatively slow, in a time window of milliseconds to seconds. As shown in Figure 1.9, the time gap between charge separation and the chemical reaction is the main reason for the low efficiency of the dye sensitized photocathode for solar fuel generation. How to slow down charge recombination and produce long-lived stable intermediates to bridge this time gap is important for realizing an efficient photocathode.

Dye or dye-catalyst assemblies with long-lived charge separation have been explored for decades. Gibson designed the triphenylamine donor–bodipy acceptor dye with long-lived charge separation. Tuning the electronic coupling by substituting bidipy sites was suggested to further increase the charge separation lifetime. Odobel designed three new iridium complexes with long-lived charge separation and they assigned it to the methylene group inserted between the phosphonic acid anchors and the phenylpyridine ligand, as well as the location of the electron spin density on the ancillary ligand. Kerlidou revealed two charge recombination paths for a ruthenium dye with different ancillary ligands and found that substitution of a bipyridine by a dipyridophenazine ligand can stabilize charge separation. Hammarström reported that the ultrafast charge recombination between a perylene imide dye and NiO lies more in the Marcus normal region, which is different from the TiO$_2$ based electrode. Therefore, they proposed that charge recombination occurs mainly to the intra-band gap states caused by bulk or surface Ni$^{2+}$ vacancies. Later on, they reported that Ni$^{2+}$ trapped holes are responsible for the slow recombination, while Ni$^{3+}$ trapped holes likely lead to fast recombination. The charge recombination could be slowed down by applying a negative potential, using chemical reductants, or passivating the surface defects to reduce the Ni$^{3+}$ state. Wasielewski reported a Al$_2$O$_3$ protection layer deposited on the dye can not only prevent the surface adsorbed dye from desorption and degradation, but also can stabilize the intermediate state by suppressing charge recombination.
1.5 Research aims and outline

The performance of a tandem DSPEC cell is hampered by the low efficiency of the photocathode. Various strategies have been proposed in order to enhance the performance. The primary limitation is that the chemical reaction occurs significantly slower than charge recombination between the NiO and the dye-catalyst assembly. Therefore, it is important to further develop fundamental insight, and based on that adjust the photocathode design.

In Chapter 2, the experimental details including sample preparation and characterization are described. In addition, the principles behind femtosecond transient absorption and time-resolved photoluminescence spectroscopy used for mechanistic studies are discussed.

In Chapter 3, the effect of Cu-doping of NiO on the photodynamics and performance is explored. It turns out that Cu-doping can slow down surface charge recombination and enhance the photocurrent of the P1 dye-sensitized photocathode. This work highlights that the nature of the NiO surface plays an important role in improving the efficiency.

In Chapter 4, the photodynamics of P1-sensitized NiO in different working environments is studied. Both fast hole injection as well as fast charge recombination are observed when the photocathode is exposed to an aqueous or humid environment. We assign this to a dual role of surface OH⁻ on the NiO, accelerating both light-induced hole injection and recombination, highlighting the importance of balancing the quantity of surface OH⁻.

In Chapter 5, the photodynamics of P1-sensitized NiO in aqueous electrolyte under different external potentials is investigated by time-resolved photoluminescence and femtosecond transient absorption. At more negative potential, charge recombination is slowed down, analogous to literature. However, hole injection appears to also be slowed down instead of being promoted. We assign this to compositional changes (H⁺ and OH⁻) in the electrochemical double layer induced by the external bias, which is in agreement with the dual function of OH⁻ as described in Chapter 4.

In the research described in Chapter 6, myristic acid with a long hydrophobic alkyl chain and a carboxylic acid anchoring group is co-adsorbed on the NiO surface with the aim to decrease the fast charge recombination between de P1 dye and NiO. In addition to control over the surface hydroxylation, the long alkyl chains also provide an apolar environment to the P1 dye molecules and inhibit the molecular twisting after photoexcitation, which appears to drive H₂ evolution from water without additional catalyst.

In Chapter 7, the preparation and analysis of a film of a new p-type material, CuBO₂, is described. The properties of the obtained CuBO₂ film are sensitive to the precursor solution and annealing conditions. The CuBO₂-based photocathode shows significantly slow charge recombination compared with the NiO-based analogue.
Chapter 8 summarizes the results and proposes further research on the dye-sensitized photocathode.

References


Chapter 1


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Introduction


CHAPTER 2

Experimental principles and details
2.1 Ultraviolet-visible (UV-vis) absorption spectroscopy

UV-vis absorption spectroscopy is a widely used spectroscopic technique to study electronic transitions in materials. Molecules can absorb photons when exposed to light, which has typically a wavelength between 200 nm and 800 nm for regular UV-vis spectroscopy. The light absorption promotes the molecule from the ground state into the excited state. Multiple electronic transitions that exist in organic molecules as shown in Figure 2.1:¹

(1) The $\sigma \rightarrow \sigma^*$ transition: $\sigma$ chemical bonds are usually very strong and require a high photon energy for electronic excitation.

(2) The $n \rightarrow \sigma^*$ transition typically requires less energy compared to the $\sigma \rightarrow \sigma^*$ transition.

(3) The $\pi \rightarrow \pi^*$ transition, very common in organic molecules, with the energy gap depending on the structure and size of a molecule and the degree of electron delocalization.

(4) The $n \rightarrow \pi^*$ transition, a commonly detected transition in the UV-vis range, but normally with a lower light absorption efficiency than e.g. the $\pi \rightarrow \pi^*$ transition.

In most organic molecules, bonding orbitals are (almost) filled and anti-bonding orbitals are typically empty; important concepts are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Due to homogeneous and inhomogeneous broadening, these electronic transitions lead to an absorption spectrum rather than narrow absorption lines.

![Figure 2.1](image.png)

**Figure 2.1.** Schematic diagram of different electronic transitions in a molecule.

By comparing the transmitted light intensity through the sample and reference (a blank does not have any absorption in the measurable range), the absorbance and light absorption efficiency can be calculated according to the equations below:

\[
T = \frac{I}{I_0} \times 100 \% \quad (2.1)
\]

\[
A = -\log T \quad (2.2)
\]
\[ F_A = (1 - 10^{-4}) \times 100 \% \]  
(2.3)

Where \( A \) is the absorbance, \( T \) the transmittance, \( F_A \) the light absorption efficiency, \( I_0 \) the intensity of the incident light and \( I \) the intensity of the transmitted light. The absorbance is proportional to the molar absorptivity (\( \epsilon \)), concentration (\( c \)) and optical path length (\( l \)) according to the Lambert–Beer law:

\[ A = \epsilon lc \]  
(2.4)

A ThermoSci EVO600 spectrometer was used to collect the UV-vis data in the following chapters. The reflectance spectrum was recorded using a PerkinElmer Lambda 950S spectrometer using an integrating sphere.

2.2 Time-resolved photoluminescence (TRPL)

2.2.1 Theory

Photoluminescence (PL) is one of the most important tools to explore excited state processes and their dynamics, as shown in Figure 2.2. When a photon with sufficient energy hits a molecule, the molecule can be excited from the ground state (\( S_0 \)) to an excited state (\( S_1, S_2 \ldots S_n \), and the vibrational energy levels thereof), during this process the electron keeps a spin opposite to the electron remaining in the ground state. This light absorption process occurs in a time range of attoseconds (~10\(^{-18}\)-10\(^{-15}\) s, 1 as = 10\(^{-18}\) s). After the electron is excited, the energy can be dissipated through a variety of pathways. Normally, vibrational relaxation (VR) is one of the first processes, taking place on a time scale of sub-picoseconds (~10\(^{-13}\)-10\(^{-12}\) s, 1 ps = 10\(^{-12}\) s), during which part of the electronic excitation energy is converted into vibrational motion. Internal conversion (IC) is a nonradiative transition between a higher and a lower electronic state (for example from \( S_2 \) to \( S_1 \)) during which the electron does not change its spin. When two electronic energy levels are close in energy, internal conversion is normally fast.\(^2\) When the electron occupies the lowest excited state \( S_1 \), it can either decay back to the \( S_0 \) state by emitting a photon referred to as photoluminescence or radiationless decay, or undergo an intersystem crossing (ISC) process from the singlet state \( S_1 \) into the triplet state \( T_1 \). The electron spin flips during the transition from \( S_1 \) to \( T_1 \) (Figure 2.2 b). As \( T_1 \) and \( S_0 \) have different electron spin multiplicity, the relaxation from \( T_1 \) to \( S_0 \) is a theoretically forbidden transition. Nevertheless, it does happen in some molecules, though with a slow rate constant. As a result, emission by a triplet state referred to as phosphorescence is normally substantially slower (~microseconds or longer) than emission by singlet states (~nanoseconds). In addition to these internal decay processes within the molecule, excited states can also decay via external processes towards other molecules in the direct environment like Förster energy transfer, electron transfer or proton transfer.\(^3\)
Figure 2.2. (a). Energy level diagram and deactivation pathways for a photoexcited molecule; (b) Electron configurations for the ground state, the singlet excited state and the triplet excited state. The thick black lines present electronic levels, the thin black lines vibrational levels.

2.2.2 Setup

The time-resolved photoluminescence was measured by a streak camera setup (Hamamatsu, C10910), using the attenuated output of a Fianium laser (FP-532-1-s, center wavelength 532 nm, pulse duration of 300 fs, 80.37 MHz repetition rate). For experiments with UV excitation (267 nm), the output was focused into a 3 mm β-BaB\(_2\)O\(_4\) crystal (Newlight Photonics). The residual 532 nm output was removed by three dichroic mirrors (Thorlabs, MBI-K04) and a FGUV11-UV filter (Thorlabs). The laser beam was focused using a quartz lens with 50 mm focal length onto the samples in a quartz cuvette (Hellma, 10 mm optical path length) filled with different substances such as air, 0.1 M phosphate buffer solution (PBS, pH=7) or anhydrous acetonitrile (Sigma-Aldrich, 99.8 %). The photoluminescence was collected using two 2-inch diameter 50 mm focal length glass lenses and focused on the input of a spectrograph (Acton SP2300, Princeton Instruments, slit width set at 100 mm) using a grating with 50 lines/mm blazed at 600 nm. The output of the spectrograph was sent to the photocathode of the streak camera. Quartz (Uqg optics) instead of e.g. glass was normally used as the substrate to avoid background photoluminescence signal with UV excitation. Before each series of experiments, the spectral calibration was checked using a Hg/Ar calibration lamp (Oriel, LSP035) and adapted if necessary. The measured PL spectra were corrected for the spectral sensitivity of the setup by comparison of the measured and provided spectrum of a black body calibration lamp (Ocean Optics, HL-2000).
2.3 Transient absorption (TA) spectroscopy

2.3.1 Theory

As described above, TRPL can only provide information about excited state processes that decay by emission. Transient absorption spectroscopy can also provide complementary information about optically dark intermediate states. TA spectroscopy is a pump-probe technique as shown in Figure 2.3a. Laser pulses from an amplified system (the fundamental) are divided by a beam splitter into an excitation path to generate the pump path with high intensity and the probe path with low intensity. The pump beam is sent into an optical parametric amplifier to produce pump pulses with tuneable wavelength, which are then attenuated and used for excitation of the sample. A broadband white light probe is generated by focusing a small portion of the fundamental into a nonlinear medium such as a CaF$_2$ crystal. Both the pump and probe pulses are focused on the same spot of the sample, with a tunable time delay between pump and the probe. A chopper wheel periodically blocks the pump beam to measure the transmission of the sample with and without excitation. Therefore, the TA spectra is in general a difference spectrum; the change in absorbance with (A$_{on}$) and without excitation (A$_{off}$) as function of the time since the excitation pulse. As described in the UV-vis spectroscopy section, the absorbance of the same sample before and after excitation can be obtained using:

\[ A_{on} = -\log \frac{I_{on}}{I_0} \]  
\[ A_{off} = -\log \frac{I_{off}}{I_0} \]  
\[ \Delta A = A_{on} - A_{off} = \log \frac{I_{off}}{I_{on}} \]  

$I_0$ is the intensity of the incident pulse and $I_{on}$ and $I_{off}$ are the transmitted light intensity with pump on and off. $\Delta A$ is the change in absorbance of the sample with and without excitation, which is the signal that is measured in the TA setup.

There are typically three kinds of signals contributing to the TA spectrum as shown in Figure 2.3 b:

(1) Ground state bleaching (GSB): As described in the UV-vis section, before excitation the molecule in the ground state has an absorption spectrum. After the molecule is promoted from the ground state to the excited state by the pump pulse, the population of molecules in the ground state decreases and leads to the less ground state absorption. Therefore, the absorbance difference $\Delta A$ has a negative value, but should in principle appear at the same wavelengths as the UV-vis absorption spectrum.

(2) Stimulated emission (SE): The SE signal appears at the same position in a spectrum as the photoluminescence. Basically, an excited molecule can return to its ground state by emitting a photon. The incoming probe with a specific frequency can interact with the molecule in the excited state and promote it to relax back to the ground state and emit a photon. The emitted photon adds to the
intensity of the transmitted light $I_{\text{on}}$, therefore, $\Delta A$ also has a negative value.

(3) Photoinduced absorption (PIA): In short, the PIA is the absorption of newly formed species. When the molecule gets promoted to the excited state, the excited molecule can be seen as a new species with new electronic transitions. Therefore, a new absorption band appears in the TA spectrum with positive $\Delta A$. Also charge transfer from the excited molecule to e.g. another molecule or semiconductor can lead to a new positive $\Delta A$ signal in the TA spectrum.

Figure 2.3. (a). Schematic diagram of TA setup; (b) the energy level of different transitions and the correlated TA signal.4

2.3.2 Setup

In this thesis, a Coherent Legend Ti:sapphire amplifier was used to produce 800 nm pulses at 5 kHz repetition rate with a pulse duration of $35 \pm 1$ fs (full width at half-maximum). The 800 nm output was split into two beams using a 90:10 beam splitter. The 500 nm pump beam was generated by sending the major part of the 800 nm beam into an optical parametric amplifier (Coherent, Opera). The white light continuum probe was produced by guiding the remaining part of the 800 nm beam through a mechanical delay stage and focusing into a CaF$_2$ crystal (Newlight Photonics, 3 mm thickness). The crystal was continuously moved to avoid thermal damage. The remaining 800 nm fundamental was removed from the probe using two 700 nm short-pass filters (Thorlabs). The polarizations of the pump and probe beams were set at 54.7° magic angle to avoid anisotropy effects.5 The pump was focused to a spot of ca. 250 μm diameter, significantly larger than the focused probe spot (ca. 100 μm diameter), and it is thus reasonable to assume that we probe a homogeneously excited sample. After passing through the sample, probe pulses were sent into a 15 cm spectrograph coupled to a home-built 256 pixels diode array detector. The differential absorbance between pump on and off was obtained by chopping the pump beam at 2.5 kHz. The time resolution is ca. 100–150 fs. The samples were mounted on a stage continuously moving with a velocity of ca. 1 mm/s to refresh the measurement.
area regularly and avoid potential charge accumulation and photodegradation. The TA signal decay in time has been verified not to be caused by potential photodegradation. The pump power was kept relatively low (∼5 × 10^{14} \text{photons/(cm}^2\text{pulse)}) and verified to be in the linear regime, i.e. the signal intensity is proportional to the number of incident photons and the normalized signal decay does not depend on the number of incident photons.

2.3.3 Data analysis

The TA spectrum requires a more complex analysis than exponential fits of the decay at a single wavelength, since normally many signals overlap at the same wavelength. Global and target analysis of the TA data was performed by using the open-source program Glotaran.

The measured TA data is a matrix \(\Psi(t, \lambda)\) which is a superposition of multiple components and each component has its own time-dependent spectrum \(\varepsilon(\lambda)\) and wavelength kinetics \(c(t)\), therefore the TA data is the sum of the products of the \(\varepsilon(\lambda)\) and \(c(t)\) for each component:

\[
\Psi(t, \lambda) = \sum_{i=1}^{n} c_i(t) \varepsilon_i(\lambda) \tag{2.8}
\]

The number of the components can be estimated using singular value decomposition (SVD):

\[
\Psi_{m\times n} = U_{m\times m} S_{m\times n} W_{n\times n}^T \tag{2.9}
\]

where \(\Psi_{m\times n}\) is the \(m\times n\) matrix representing the TA spectra, while \(U\) and \(W\) are \(m\times m\) and \(n\times n\) orthogonal matrices. The columns of \(U\) and \(W\) represent the left and right singular vectors, respectively. \(S\) represents the \(m\times n\) diagonal matrix and the element \(S_i\) in \(S\) is the singular value of \(\Psi_{m\times n}\). The number of the components is the number of singular values. Considering experimental noise in the data, only singular values with significant difference are taken into account. In addition, each component should have a physical meaning.

After the number of the components has been estimated, global analysis can be carried out to get information about the individual spectra and kinetics. As shown in Figure 2.4, in the parallel model each component decays in parallel, the derived spectra are called decay associated spectra (DAS). As an alternative, a sequential model can be used when each component decays into the subsequent component, the corresponding spectra are referred to as evolution associated spectra (EAS). However, in reality, the decay paths are usually more complicated. For example, the component A might decay into B and C, and then B and C decay to the ground state independently. In this way, even though it may still be a simplification, we need to establish a more complex photophysical model that is closer to reality. This is called target analysis, and the corresponding spectra are called species associated spectra (SAS).
Figure 2.4. Schematic diagram of different models used to achieve a fit to the TA data.

2.4 Electron transfer (ET) theory

The theory for electron transfer (ET) is extensively discussed in the literature and essential to explain chemical reactions. There are two types of electron transfer:

(1) outer sphere ET.

(2) inner sphere ET.

The outer sphere ET occurs between two separate complexes without electronic coupling, therefore it is a long distance hopping process. In contrast, in inner sphere ET, a ligand acts as a bridge between the donor and acceptor complex and promotes the ET process. Examples of outer and inner sphere ET are reactions 1 and 2, where the chloride in reaction 2 acts as a bridging ligand. The inner sphere ET rate is typically 9 orders of magnitude faster than outer sphere ET.

Reaction 1: $\text{Co(NH}_3\text{)}_6^{3+} + \text{Cr}^{2+} \rightarrow \text{Co}^{2+} + \text{Cr}^{3+} + 6 \text{NH}_3 \ k=10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

Reaction 2: $\text{Co(NH}_3\text{)}_5\text{Cl}^{2+} + \text{Cr}^{2+} \rightarrow \text{Co}^{2+} + \text{CrCl}^{2+} + 6 \text{NH}_3 \ k=6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$

The Marcus theory for ET was developed by Rudolph A. Marcus to explain the rate of outer sphere ET reactions in 1956 and extended to various conditions later. The parabolas in Figure 2.5 are usually used to describe the Marcus theory. The ET barrier and rate can be estimated from the equations below:
\[
\Delta G^\# = \frac{(\Delta G^0 + \lambda)^2}{4\lambda}
\]  
\[k_{ET} = \frac{\frac{3}{2\pi^2}}{h\sqrt{\lambda k_BT}} (V)^2 \exp \left( \frac{-\Delta G^\#}{k_BT} \right)
\]

Where \(\Delta G^\#\) is the activation energy for electron transfer, \(h\) is Planck constant and \(k_B\) is the Boltzmann constant. According to this theory, the ET rate \((k_{ET})\) is determined by the electronic coupling \((V)\) between donor \((D)\) and acceptor \((A)\), the reorganization energy \((\lambda)\), the Gibbs free energy \((\Delta G^0)\) and the temperature \((T)\). As shown in Figure 2.5, there are three Marcus regions:

The normal region, where \(\lambda > -\Delta G^0\), the ET rate increases with larger driving force.

The optimal region, where \(\lambda = -\Delta G^0\), the activation energy is 0 and the ET rate is maximum.

The inverted region, where \(\lambda < -\Delta G^0\), the ET rate decreases with an increase in driving force.

**Figure 2.5.** Potential energy surfaces for light-induced electron transfer between donor \((D)\) and acceptor \((A)\) in the normal, optimal and inverted regime of the Marcus theory. \(\Delta G^\#\) is the activation energy for electron transfer, \(\Delta G^0\) is the overall Gibbs free energy and \(\lambda\) is the reorganization energy.

### 2.5 Photoelectrochemical (PEC) and in-situ TRPL and TA measurements

All the photoelectrochemical measurements in this thesis were carried out in the three electrodes cell shown in Figure 2.6 a and b. The cell has three parts: the main chamber, the sample holder with different window sizes for different sample sizes, and a cap with screws. The samples are deposited onto fluorine doped tin oxide (FTO), while Cu tape was used as the working electrode, an Au wire as the counter electrode and Ag/AgCl as the reference electrode. The PEC cell was placed in a position where the light intensity is 1 sun (100 mW/cm²) with AM 1.5 global filter and UV filter (blocking
below 400 nm), and the light intensity was calibrated by using a standard Si solar cell. The back side of the cell is equipped with a quartz glass, which allows illumination from the either the front side or back side of the cell. In this research, the illumination was from the front side (back side of the sample), unless specified differently.

A 1×1 cm quartz (PL measurement) or 1×1 cm PMMA cuvette and a portable potentiostat were used for the in-situ TA and PL measurements (Figures 2.6 c and d). The sample is extended by a Cu tape as a working electrode and placed in parallel to the cuvette for TA and at ~45° for PL. The reference and counter electrodes were placed at the side of the sample while avoiding contacting each other. The electrolyte was then injected slowly to ensure that the three electrodes were immersed, but not in contact with the Cu tape. Then the electrical potential was set by using chronoa amperometry. Finally, the TA or PL measurement was started as usual after stabilization of the current.

**Figure 2.6.** (a, b) Digital photos of the PEC cell, (c) Schematic diagram of the PEC cell and (d) the digital photo of potentiostat used for in-situ TA or PL measurement.

The photocurrent density (j) is frequently used as a performance evaluation criterion in PEC cells. In two-electrode containing PEC cells for water splitting, the efficiency can be calculated from the photocurrent density using the equation:\textsuperscript{15}

\[
\eta_{\text{STH}} = \frac{j \times (V_{\text{O}_2} - V_{\text{app}})}{P_{\text{total}}} \eta_F
\] \hspace{1cm} (2.12)

Here \(\eta_{\text{STH}}\) is the solar to hydrogen efficiency, \(\eta_F\) is the Faraday efficiency and \(P_{\text{total}}\) is the power density of the incident light. The half-cell efficiency as function of applied potential (\(V_{\text{app}}\)) can be calculated in a system consisting of three electrodes from the equations:

**Photoanodes:** \[
\eta_{\text{O}_2} = \frac{j \times (V_{\text{O}_2} - V_{\text{app}})}{P_{\text{total}}} \times \eta_F = \frac{j \times (1.23 V - V_{\text{app}})}{P_{\text{total}}} \times \eta_F
\] \hspace{1cm} (2.13)
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Photocathodes: \[ \eta_{H_2} = \frac{j \cdot (mA/cm^2) \cdot (V_{app} - V_{H_2})}{P_{total}(mW/cm^2)} \times \eta_F = \frac{j \cdot (mA/cm^2) \cdot V_{app}}{P_{total}(mW/cm^2)} \times \eta_F \] (2.14)

Usually, the overall efficiency is the product of light absorption efficiency (\( \eta_{abs} \)), charge separation efficiency (\( \eta_{sep} \)) and charge injection efficiency (\( \eta_{inj} \)):

\[ \eta = \eta_{abs} \times \eta_{sep} \times \eta_{inj} \] (2.15)

The light absorption efficiency can be obtained from the UV-vis spectra. The quantification of the charge separation efficiency is challenging, but it can be qualitatively obtained from the decay of the transient absorption signals. Usually, the \( \eta_{inj} \) value is assumed to equal 1 when a high concentration of hole or electron scavenger is present in the electrolyte.

References

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Dye-sensitized photoelectrochemical DSPEC water splitting is an attractive approach to convert and store solar energy into chemical bonds. However, the solar conversion efficiency of a DSPEC cell is typically low due to a poor performance of the photocathode. Here we demonstrate that Cu-doping improves the performance of a functionalized NiO-based photocathode significantly. Femtosecond transient absorption experiments show longer-lived photoinduced charge separation for the Cu:NiO-based photocathode relative to the undoped analogue. We present a photophysical model that distinguishes between surface and bulk charge recombination, with the first process in the time range of 10 ps occurring more than one order of magnitude faster than the latter. The longer-lived photoinduced charge separation in the Cu:NiO-based photocathode likely originates from less dominant surface recombination, and an increased probability for holes to escape into the bulk and to be transported to the electrical contact of the photocathode. Cu-doping of NiO shows promise to suppress detrimental surface charge recombination and to realize more efficient photocathodes.
3.1 Introduction

Solar energy is an inexhaustible and clean energy source and has great potential to replace fossil fuels. Dye-sensitized photoelectrochemical DSPEC cells are attractive due to their ability to convert solar energy into H₂ by water splitting or other fuels by CO₂ reduction.¹⁻³ In a typical p-n tandem DSPEC cell, both photoanode and photocathode consist of a semiconductor sensitized with a light-absorbing dye and a catalyst. The semiconductor layer is generally nanoporous to ensure a large surface area for abundant dye and catalyst adsorption. The photoanode performs the oxidation reaction and the photocathode the reduction reaction.⁴ The photocathode has attracted less attention compared to the photoanode⁵ and limits the DSPEC performance, with reported incident photon-to-current efficacies of <1% for NiO-based photocathodes vs. ~25% for TiO₂-based photoanodes.⁶⁻⁹ Hence, the development of an efficient photocathode is crucial for improving the overall performance of DSPEC cells.

The electronic energy levels and chemical stability make NiO a promising p-type semiconductor for application in dye-sensitized photocathodes.¹⁰ Despite the numerous strategies investigated, with particular focus on the design of new dyes and catalysts, improving the performance of NiO-based photocathodes remains a challenge.¹¹⁻¹³ Light-induced ultrafast hole injection from the dye into the NiO should be followed by electron transfer from the dye to the catalyst, enabling the catalytic reduction reaction and restoring the light absorbing capability of the dye. However, the photocathode performance is in general limited by fast charge recombination from the NiO back to the dye radical anion, occurring normally even prior to the vital electron transfer step from the dye to the catalyst.¹⁴ Hammarström et al. reported ultrafast <150 fs hole injection from a coumarin dye C343 into NiO followed by a ~9 ps charge recombination process.¹⁵ Wu et al. observed <200 fs hole injection for triphenylamine-oligothiophene-perylenemonoimide sensitized NiO followed by fast tens of ps to several μs charge recombination.¹⁶ For NiO sensitized with the dye 4-bis-4-[5-2,2-dicyano-vinyl-thiophene-2-yl]-phenyl-amino-benzoic acid P1, hole injection was found to occur in ~230 fs with also some slower a few ps hole injection, followed by different recombination pathways ~2.7 ps, ~17 ps and ~205 ps.¹⁷

In addition to the dye and catalyst design, the properties of the NiO and in particular surface defects are likely to play an important role in the fast charge recombination often observed.¹⁸⁻²⁰ Unlike the dye and catalyst, modification of NiO has however gained less attention so far,³²¹ although Li⁺,²²,²³ Mg²⁺,²⁴,²⁵ and Co²⁺²⁶ doping have been investigated by a number of groups and were observed to reduce charge recombination between NiO and dye. The bandgap of NiO of 3.4 - 4.0 eV is assigned to the O 2p → Ni 3d electronic transition.²⁷⁻³⁰ The intrinsic p-type character of NiO is generally accepted to originate from the presence of Ni vacancies where holes could localize.²⁸ Holes are likely surrounded by self-induced lattice distortions polarons, and this self-trapping is hampering hole
As a result, holes injected by the photoexcited dye may remain at the NiO surface, which in turn likely promotes charge recombination with the dye radical anion. Improving hole transport could be a promising strategy to prevent undesirable interface charge recombination.

As previously mentioned, P1 has been especially designed for photosensitization of NiO and other p-type semiconductors. In this work, we explore the potential of nanoporous Cu-doped NiO layers prepared by sol-gel methods for DSPEC solar water splitting and observe an enhancement in photocurrent for P1-photosensitized Cu: NiO layers relative to analogues based on NiO. The strongest improvement is observed for 9 mol% doped Cu: NiO/P1 photocathodes. The photodynamics responsible for this effect have been investigated by femtosecond transient absorption spectroscopy. Cu-doping appears to reduce ultrafast charge recombination, which we discuss in terms of different hole transport in NiO and Cu:NiO layers. We demonstrate that Cu-doping is a promising strategy to overcome the current limitation of NiO-based photocathodes and holds promise for efficient photocatalytic conversion.

3.2 Experimental

3.2.1 Preparation of photosensitized NiO and Cu: NiO films

The NiO and Cu: NiO films were prepared by spin-coating. The precursor solution for NiO was prepared by dissolving 0.3 M Ni(NO$_3$)$_2$ • 6 H$_2$O 99.999 %, Sigma-Aldrich and polyvinyl acetate 0.05 g/ml, Sigma-Aldrich into methanol Sigma-Aldrich, >99.9 %. The precursor solution was aged for more than 1 day prior to spin-coating. For the Cu: NiO precursor, the total concentration of Ni(NO$_3$)$_2$ • 6H$_2$O and Cu(NO$_3$)$_2$ >99 %, Sigma-Aldrich together was 0.3 M. The precursor solution was spin-coated onto a cleaned FTO substrate cleaned by acetone, isopropanol and ethanol fluorine-doped tin oxide, Biotain crystal in two spinning steps: 0 rpm for 10 s and 3000 rpm for 20 s. After spin-coating of each layer, the films were dried at 300 °C in air for 10 min. The thicknesses of the NiO and Cu: NiO films were controlled by repeating the spin-coating and drying processes for three times. The films were finally calcined at 450 °C in air for 60 min. The as-prepared NiO and Cu: NiO films were soaked in 0.3 mM 4-bis-4-[5-2,2-dicyano-vinyl-thiophene-2-yl]-phenyl-amino-benzoic acid P1 dye solution in ethanol overnight ~16 h and washed by ethanol.

3.2.2 Sample characterization

The crystal structures were determined by X-ray diffraction XRD Bruker D2, Cu Kα source. The nanomorphology of the layers were studied by a Zeiss MERLIN HR-SEM. The UV–Vis spectra of the films were collected in transmission mode using a ThermoSci EVO600 spectrometer.

3.2.3 Femtosecond transient absorption spectroscopy fs TA

The fs TA experiments were carried out on the dry film in air. A Coherent Legend Ti:Sapphire
amplifier was used to produce 800 nm pulses at 5 kHz repetition rate with a pulse duration of 35±1 fs full width at half maximum. The 800 nm output was split into two beams using a 90:10 beam splitter. The 500 nm pump beam was generated by sending the major part of the 800 nm beam into an optical parametric amplifier Coherent, Opera. The white light continuum probe was produced by guiding the remaining part of the 800 nm beam through a mechanical delay stage and focusing into a CaF₂ crystal Newlight Photonics, 3 mm thickness. The crystal was continuously moved to avoid thermal damage. The remaining 800 nm fundamental was removed from the probe by using two 700 nm short-pass filters. The polarizations of the pump and probe beams were set at 54.7° magic angle to avoid anisotropy effects. The pump was focused to a spot of ca. 250 μm diameter, significantly larger than the focused probe spot ca. 100 μm diameter and it is thus reasonable to assume that we probe a homogeneously excited sample. After passing through the sample, the probe pulses were sent into a 15 cm spectrograph coupled to a home-built 256 pixels diode array detector. The differential absorbance between pump on and off was obtained by chopping the pump beam at 2.5 kHz. The time resolution is ca. 100–150 fs. The samples were mounted on a continuously moving stage with a velocity of ca. 1 mm/s to refresh the measurement area regularly and avoid potential charge accumulation and photodegradation. The pump signal decay in time has been verified to not be caused by potential photodegradation. The pump power was kept relatively low ~5 x 10¹⁴ photons/cm² pulse and verified to be in the linear regime. Samples were checked for photodegradation by comparing UV-Vis absorbance spectra before and after the TA measurements and no changes were observed. The data were analysed using the open-source program Glotaran.³⁵

3.2.4 Photoelectrochemical measurements

Photoelectrochemical PEC measurements were carried out in a three-electrode cell using an electrochemical analyzer VersaSTAT 3 Potentiostat Galvanostat under illumination by a solar simulator with AM 1.5G filter Newport. The input light intensity was adjusted to 1 sun with a filter supplier filter, cutting off UV below 400 nm. The as-prepared films were used as the working electrode, and a gold wire and a Ag/AgCl electrode saturated with 3 M NaCl acted as the counter and reference electrodes, respectively. A 0.1 M phosphate buffer solution PBS, pH = 7 was used as the electrolyte, and 0.05 M K₂S₂O₈ was used as electron sacrificial agent. All the PEC cells were degassed by N₂ for more than 20 min. before the photoelectrochemical measurements. The scan direction is from high to low potential with a scan rate of 5 mV/s.
3.3 Results and discussion

Fig. 1 shows the surface morphology and cross-section of NiO and 9 mol% Cu:NiO films on FTO/glass substrates. 9 mol% doping gives the largest enhancement in photocurrent, see Fig. S1 of the supporting information. Energy-dispersive X-ray spectroscopy analysis EDS, Fig. S2 confirms the Cu percentage in the film ~8.2 mol% is quite close to the 9 mol% in the precursor solution. For both the NiO and Cu:NiO films, nanoparticles have sintered together into a nanoporous structure, and Cu-doping does not have a significant effect on the morphology. The layer thickness of both samples is around 240-245 nm, significantly thinner compared to many other studies. Nevertheless, strong visible light absorption is achieved for these layers sensitized with P1 dye see Fig. 2, likely due to the small particle size and the porous nature of these layers, which increases the surface area for P1 adsorption, and therefore the quantity of P1.
Unraveling the Mechanisms of Beneficial Cu-Doping of NiO-Based Photocathodes

Figure 2. a XRD patterns of NiO and 9 mol% Cu: NiO layers on glass causing the broad diffraction line around $2\theta = 20$–30$^\circ$; b UV-Vis spectra of the layers with and without P1 dye.

Fig. 2a shows the XRD patterns of NiO and 9 mol% Cu: NiO layers; the data for layers with different mol% Cu-doping are shown in Fig. S4 of the supporting information. Since the FTO used as transparent conducting electrode shows strong XRD lines, partially overlapping with those of NiO, we have used amorphous glass as the substrate for XRD analysis to observe trends induced by doping in detail. All the layers show two diffraction lines at around 2θ values of 37° and 47°, which correspond to the 111 and 200 facets of cubic NiO according to the XRD JCPDS card number PDF#47-1049. No Cu-related separate phases like CuO and Cu$_2$O are observed, which is consistent with the literature. Calculations of the crystallite size and interplanar spacing based on the Scherrer equation and Bragg’s law are provided in Fig. S5 and Table S1 of the supporting information. This analysis indicates a smaller crystallite size for Cu: NiO layers, possibly due to the strain caused by the slightly larger ionic radii of Cu$^+$ or Cu$^{2+}$ ions, causing a decrease in XRD peak intensities. Substitution of Ni$^{2+}$ ions by Cu$^+$ or Cu$^{2+}$ ions also result in an increase in interplanar spacing and lattice parameter, in agreement with earlier work. X-ray photoelectron spectroscopy XPS, Fig. S3 indicates a Cu doping percentage of ca. 8.1 mol%, in agreement with EDX analysis. Furthermore, the XPS data show that Cu$^+$ and Cu$^{2+}$ coexist in the film.

Fig. 2b shows the UV-Vis absorbance spectra of bare NiO and 9 mol% Cu: NiO films and the layers photosensitized with P1 dye. The UV-Vis absorbance spectra of Cu-doped NiO layers with different mol% doping, and the fraction of absorbed light as function of wavelength are shown in Figs. S6 and S7 of the supporting information. The bare NiO layers show some absorbance in the visible, likely due to trap states and a steep rise in absorbance <350 nm. Tauc analysis supporting information Fig. S8 gives a small decrease in bandgap for 9 mol% Cu: NiO, possibly due to a change in nature of the valence band, which effect will be discussed below. The increased absorbance in the visible indicates the presence of Cu-induced levels in the bandgap, in agreement with earlier work reporting a decrease in transmission in the visible induced by Cu-doping.
P1 in acetonitrile is known to show a strong absorbance in the visible due to a π - π* transition, with a maximum extinction coefficient of $5.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 468 nm. Relative to P1 in solution, the P1 sensitized Cu:NiO films show a broadening and red-shift in absorbance, likely due to structural inhomogeneity and electronic coupling between dye and semiconductor, with a maximum around 500 nm as observed earlier see Fig. 2b. The visible light absorbance of 9 mol% Cu:NiO/P1 is higher than for equivalently prepared NiO/P1 analogues, which is likely due to a larger electrochemically active surface enabling adsorption of higher quantities of dye Fig. S9 supporting information.

**Figure 3.** Photoelectrochemical performance with chopped illumination with 1 sun AM 1.5G, >400 nm of NiO/P1 and 9 mol% Cu:NiO/P1 photocathodes. a In 0.1 M phosphate buffer solution PBS at pH = 7 scan from high 0.7 V to low potential 0 V with a rate of 5 mV/s to 0 V vs RHE and b at 0.31 V bias voltage vs. reversible hydrogen electrode RHE; c in 0.1 M PBS with 0.05 M K$_2$S$_2$O$_8$ as electron scavenger, again scanning from 0.7 V to 0 V with 5 mV/s. Prior to the measurements, the solutions were degassed with N$_2$ for at least 20 min.

The photoelectrochemical performance was measured in a three-electrode cell configuration under irradiation of a solar simulator sent through a chopper and UV filter blocking wavelengths <400 nm. The Cu:NiO/P1 photocathode in 0.1 M phosphate buffer at pH = 7 shows a higher absolute photocurrent at various applied potentials than the undoped analogue Fig. 3a, with the strongest
improvement observed for 9 mol% Cu-doping. The photocurrents significantly exceed those of the layers without P1 supporting information Fig. S10, demonstrating the photocurrent mainly originates from P1 photoexcitation. For the Cu-doped sample, the photocurrent and dark current maximizes at ~150 µA at around 0.45 V_RHE. This current is likely the consequence of the reduction of Cu^{2+} to Cu^{+} see cyclic voltammograms in Fig. S11 of the supporting information, and is likely superimposed on the transient photocurrent response induced by P1 excitation. Further, both samples show an obvious transient photocurrent the positive and negative spikes upon light-on or light-off, which is likely caused by the pseudocapacitive character of the films, including electron storage by Ni^{3+} and Cu^{2+}, and hole storage by Ni^{2+} and Cu^{+}. In addition to the enhancement in photocurrent, for the Cu-doped analogue these transient photocurrents are of higher intensity, which suggests charge storage in the Cu site is significant. This assignment is supported by the absence of a transient photocurrent in the presence of an electron scavenger Fig. 3c. An unexpected trend in Fig. 3c is the lower photocurrent at low bias potential e.g. at 0.05 V vs. RHE compared to higher potential, which seems counterintuitive as the first implies a higher driving force for photoinduced charge separation and transport. This is not only observed in this work, but also for other NiO-based photocathodes in the literature; the reason is not discussed. As both the Cu-doped photocathodes and the undoped analogues show this trend, it is possibly caused by a change in NiO oxidation states with varying applied bias potential, affecting hole transport.

The photocurrent in time of both photocathodes shows a decrease in the initial 3 minutes, but then stabilizes. For the Cu:NiO-based photocathode the photocurrent especially during the initial 3 minutes may partly originate from Cu reduction. However, after this initial stabilization time both photocathodes show a stable photocurrent, with the Cu:NiO-based photocathode steadily outperforming the NiO-based analogue ~13 µA/cm² for NiO/P1 and ~24 µA/cm² for 9 mol% Cu:NiO/P1 at 0.31 V vs. RHE. The stability is significantly higher than reported in earlier work Fig. 3b, possibly due to the thinner NiO layers used here, lowering the probability of hole accumulation. Accumulated holes at Ni sites could cause self-oxidation reactions from Ni^{2+} to Ni^{3+} or Ni^{4+}, which may diminish the performance of the photocathode. Ni^{3+} centers in NiO are known to cause a broadband absorbance in the visible, which will compete with dye molecules for light absorption and may lead to a decrease in photocurrent. After the stability test, the visible light absorbance and photocurrent both show a decrease compared with the freshly prepared photocathodes supporting information Fig. S12, which is presumably due to the P1 dye degradation or desorption in the initial 3 minutes. Compared to the freshly prepared NiO/P1, 9 mol% Cu:NiO/P1 after the stability test shows a lower light absorption but still a higher photocurrent, demonstrating a different origin of the Cu-doping induced enhancement in photocurrent.

The photoconversion efficiency mainly depends on three factors: i light absorption efficiency, ii
electron injection efficiency from dye to electrolyte and charge separation efficiency between dye and NiO.\textsuperscript{35,36} The light absorption efficiency is not the reason for the enhancement as mentioned above. In order to decouple electron injection efficiency and charge separation efficiency, photocurrents were measured under similar conditions as in Fig. 3a, but now with K$_2$S$_2$O$_8$ as electron scavenger Fig. 3c.\textsuperscript{57,58} In this situation, all electrons photoexcited to the P1 LUMO are assumed to be captured by the electron scavenger leading to formation of sulfate, SO$_4^{2-}$ and the electron injection efficiency is assumed to equal unity. The high background current in the presence of the electron scavenger is probably due to reduction of S$_2$O$_8^{2-}$. Since the difference in photocurrent induced by Cu-doping of the NiO remains, it should mainly originate from a difference in charge separation efficiency between the photoexcited dye and the NiO or Cu:NiO.

The consistent improvement in photocurrent indicates a higher charge separation efficiency for the Cu:NiO/P1 photocathode, which has been further unraveled by fs transient absorption TA spectroscopy, on the basis of which we will further explain the charge transfer processes involved after light absorption.

**Figure 4.** Transient absorption spectra at 500 nm excitation for a NiO/P1 and b 9 mol% Cu:NiO/P1. Kinetic traces for c NiO/P1 at 536 nm and 556 nm and d NiO/P1 and 9 mol% Cu:NiO/P1 at 618 nm and 646 nm. The lines indicate fits from target analysis.
Figs. 4a and 4b show the fs TA spectra at various time delays of NiO/P1 and 9 mol% Cu: NiO/P1 photocathodes at 500 nm excitation and fits from photophysical modeling see below. Both spectra show a broad positive band centered around 615 nm, red-shifting in time. Furthermore, a negative band is observed below ca. 600 nm due to ground state bleach GSB of P1. The broad absorption band around 615 nm likely represents the P1 radical anion P1•- formed after hole injection into NiO. In addition, the P1 excited state P1* is known to give rise to an excited state absorption band around 550 nm. Also redox processes in the NiO leading to Ni3+ and Ni4+ centers, such as ultrafast sub-ps hole trapping at Ni3+ sites, could lead to a transient signal in the visible. The absence of significant P1* stimulated emission around 660 nm even early after photoexcitation 150 fs, suggests ultrafast hole injection, in agreement with literature values ranging from ~200 fs – few ps. The decay of the TA signals shows charge recombination to predominantly occur on a ps timescale.

Figs. 4c and 4d show the kinetic traces at key wavelengths for NiO/P1 and 9 mol% Cu: NiO/P1 photocathodes. All transients fully develop within the instrumental response time 100-150 fs. Comparison of the traces e.g. at 536 nm and 556 nm for NiO/P1 Fig. 4c, supporting information Fig. S13 for Cu: NiO/P1 shows a more dominant contribution of P1* absorption relative to GSB at 556 nm, resulting in a less negative transient signal. The vanishing difference between the traces in time indicates that P1* decays to P1•- by hole injection into NiO in a few ps, explaining the simultaneous red-shift in the TA spectrum Figs. 4a and b. The kinetic traces at 618 nm and 646 nm Fig. 4d are indicative of P1•-, the full development of these traces within the instrumental response time indicates significant hole injection within 100-150 fs. Also trapped holes giving rise to Ni3+ or Ni4+ centers are likely to contribute to these transients. Apparently, hole injection occurs either ultrafast or in a few ps, which biphasic behavior has been observed earlier. Comparison of the early-time first few ps spectra show a slower decay for the 9 mol% Cu: NiO/P1 photocathode, indicating longer-lived charge separation.

To account for the complexity in TA data and spectral overlap in signals, target analysis of the spectrotemporal behavior has been performed using the photophysical model shown in Fig. 5. Hole injection by P1* occurs partly within the instrumental response time and in addition via a ca. 1 ps channel τ1. Furthermore, ultrafast sub-ps charge trapping at Ni2+, Ni3+ or Ni4+ sites observed earlier to result in a long-lived 200 ns broadband transient signal is considered. Three parallel charge recombination processes are needed to get a good fit τ2, τ3, τ4 for which a photophysical interpretation will be discussed below. Although this model is likely a simplification of the reality, it describes the TA data well, however, note that some charge recombination may already occur before hole injection is finalized. Table 1 presents the obtained lifetimes, the species associated spectra corresponding to τ1, τ2 are provided in Fig. S14 of the supporting information. The values for τ1, τ2 and τ3 for 9 mol% Cu: NiO/P1 photocathodes exceed those for NiO/P1 analogues, indicating both slower hole injection
not beneficial and slower charge carrier recombination for Cu: NiO/P1 the reason for the enhanced performance.

**Table 1.** Lifetimes of NiO/P1 and 9 mol% Cu: NiO/P1 from target analysis, the species associated spectra are provided in Fig. S14 of the supporting information.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$ fs</th>
<th>$\tau_2$ ps</th>
<th>$\tau_3$ ps</th>
<th>$\tau_4$ ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO/P1</td>
<td>868±20</td>
<td>8.6±0.2</td>
<td>82.9±2.2</td>
<td>$\infty$</td>
</tr>
<tr>
<td>9 mol% Cu: NiO/P1</td>
<td>1441±30</td>
<td>13.1±0.4</td>
<td>174.1±11.8</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

**Figure 5.** Simplified photophysical model for light-induced hole injection, hole diffusion, trapping and electron-hole recombination in NiO/P1 and Cu: NiO/P1 photocathodes, IRT = instrumental response time.

The Cu-induced enhancement in $\tau_1$, $\tau_2$ and $\tau_3$ likely arise from a change in valence band electronic structure, which may also be responsible for the lowering in bandgap Fig. S8 supporting information. The valence band maximum VBM of NiO is generally assigned to O 2p orbitals; the strongly localized character of these orbitals likely causes injected holes to be pinned at the NiO surface. The low mobility of holes in NiO due to their strong interaction with the lattice, leading to self-trapping and polaron formation, hinders diffusion from the surface into the bulk. Theoretical work shows that Cu-doping changes the VBM from O 2p orbitals to hybridized Cu 3d and O 2p orbitals, lowering the hole polaron hopping activation energy from 0.58 eV to 0.24 eV, and giving rise to a drastic lowering in electrical resistivity. It may also shift the VBM, as observed by Mott-Schottky experiments, and hence the driving force for hole injection from P1. Also the co-existence of Cu$^{3+}$ and Cu$^+$ ions, as
follows from XPS supporting information Fig. S3, may play a role. The presence of Cu\(^{+}\) ions can be expected to be compensated by a higher concentration of Ni\(^{3+}\) ions. The decrease in Ni\(^{2+}\) concentration likely also contributes to the slower hole injection observed for Cu-doped photocathodes.

NiO is an antiferromagnetic material and the introduction of Cu\(^{2+}\) and Cu\(^{+}\) ions into the lattice likely changes spin-charge-lattice interactions. Cu-doping of TiO\(_2\) has recently been reported to result in a large difference in charge transport dynamics for the spin-up and spin-down channels\(^6\), which may also occur here. Holes in intrinsic NiO likely localize at Ni sites\(^3\). When a hole is injected into Cu:NiO and is localized at a Ni site, this interacts with a Cu ion in the vicinity and the Cu magnetic moment may flip, forming a spin polaron\(^6\). Depending on the hole localization, such interaction may also favor hole delocalization and transport, and increase the escape probability from the surface into the bulk, which is essential to reach the TCO electrode. On the contrary, for holes localized close to Cu ions like in CuO, strong spin-charge-lattice interactions are proposed to lead to strong hole trapping and poor hole transport\(^6\). In highly doped Cu:NiO, holes behave more akin to CuO than NiO, with hole localization occurring close to Cu sites rather than Ni sites; this may explain why an optimum photocurrent enhancement was found for 9 mol\% Cu-doping supporting information Fig. S1. Also the decrease in crystallite size due to Cu-doping supporting information Fig. S5 and Table 1 may contribute to this optimum.

As NiO is a well-known material used as supercapacitor, it has the ability to store charges at the interface between NiO and electrolyte\(^6\). We investigated the open circuit voltage in time of NiO and Cu:NiO after being positively charged at 0.8 V vs. Ag/AgCl for 40 seconds supporting information Fig. S15, with NiO showing a slower decay indicative of good charge storage ability\(^6\). However, for dye-sensitized layers hole storage at the NiO surface will promote recombination after hole injection by the P1 dye, which could explain the slower charge recombination and higher photocurrent for Cu:NiO/P1.

Based on these studies above, we distinguish two parallel processes: fast recombination of P1\(^{•-}\) with immobile holes trapped at the Cu:NiO surface \(\tau_2\) and slow recombination of P1\(^{•-}\) with mobile holes able to diffuse from the surface into the bulk and vice versa \(\tau_3\). Furthermore, we assign the non-decaying component \(\tau_4\) to long-lived trapped holes, which could lead to the formation of Ni\(^{3+}\) and Ni\(^{4+}\) centers absorbing in the visible\(^5\). Relative to the undoped analogue, the 9 mol\% Cu-doped photocathode shows higher values for \(\tau_2\) and \(\tau_3\) Table 1. These effects likely arise from the Cu-induced effect on the VBM discussed above, favoring hole delocalization and diffusion, and prolonging charge separation. As a result, injected holes have a higher probability to reach the TCO electrode, leading to the significant enhancements in photocurrent observed here.
3.4 Conclusions

In the present work we report photocurrents up to ~28 μA/cm² at 0.05 V vs. RHE for functionalized NiO-based photocathodes without catalyst, substantially higher than values generally reported in the literature. Furthermore, we demonstrate a significant enhancement in photocurrent by Cu-doping of NiO, with the most pronounced increase observed for 9 mol% doping. Femtosecond transient absorption studies show that Cu-doping slows down detrimental charge recombination, likely due to stronger hole delocalization enabling holes to more easily escape from the NiO surface into the bulk. Cu-doping of NiO-based photocathodes offers the prospect to circumvent detrimental fast charge recombination by tackling the hole diffusion bottleneck of NiO, enabling a promising increase in photocatalytic performance.
3.5 Questions remaining:

3.5.1 Surface or bulk limitation?

The femtosecond TA results show that Cu doping slows down both surface and bulk charge recombination with the P1 dye. However, it is still unclear whether the PEC performance enhancement realized by Cu doping is primarily due to surface or bulk phase changes, or both. A simple experiment has therefore been carried out, which highlights the importance of the NiO surface rather than the bulk.

![Graph showing PEC performance](image)

**Figure 6.** Photoelectrochemical performance with chopped illumination with 1 sun AM 1.5G, >400 nm of photocathodes with different top layers in 0.1 M PBS with 0.05 M K₂S₂O₈ as electron scavenger, again scanning from 0.7 V to 0 V with a scan rate of 5 mV/s.

During the sample preparation process, the spin-coating and drying processes were repeated for three times by using the same precursor solution. The surface composition of the NiO can be changed by adjusting the precursor solution for the third spin coating step. In this way, samples with bulk NiO and surface Cu:NiO, or bulk Cu:NiO with surface NiO can be obtained. Figure 6 presents the PEC performance of P1 sensitized electrodes with different surface layers. It is obvious that regardless whether the bulk composition is NiO or Cu:NiO, the photocurrent density is higher for the sample with the Cu:NiO surface layer. On the contrary, the photocurrent density is lower in case of the NiO surface layer, providing evidence that the surface structure is likely more crucial for the PEC performance of a dye-sensitized NiO photocathode than the bulk composition.

3.5.2 Contradictory results for aqueous PEC and non-aqueous DSSC performance?

Based on the TA results measured in air and the PEC performance measured in the PBS electrolyte, it is reasonable to expect that Cu:NiO/P1 may also exhibit superior DSSC performance in comparison to NiO/P1. However, the opposite is observed as shown in Table 2, i.e. Cu:NiO/P1 exhibits a lower
DSSC performance. In addition, NiO/P1 with different NiO layer thickness also shows contradictory results between the PEC and DSSC performance, compare Figure 7 and Table 3. The thicker NiO film leads to a higher dye loading and higher DSSC performance. However, the PEC performance is not consistent with this trend. Both thick and thin NiO/P1 show a lower photocurrent density. Another feature worth mentioning is that the photocurrent density of the DSSC in the mA/cm² region is significantly higher than that of the same NiO based electrode in a PEC cell in the μA/cm² region, even in the presence of an electron scavenger. The working environment appears to have a significant impact on the NiO surface structure, which we will discuss further in the next chapter.

Table 2. The DSSC performance of NiO/P1 and Cu:NiO/P1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>V_{OC} mV</th>
<th>J_{SC} mA cm(^{-2})</th>
<th>Fill factor</th>
<th>Power-to-current efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO/P1</td>
<td>116</td>
<td>-1.41</td>
<td>0.332</td>
<td>0.054</td>
</tr>
<tr>
<td>NiO/P1</td>
<td>120</td>
<td>-1.61</td>
<td>0.341</td>
<td>0.063</td>
</tr>
<tr>
<td>NiO/P1</td>
<td>114</td>
<td>-1.53</td>
<td>0.333</td>
<td>0.058</td>
</tr>
<tr>
<td>NiO/P1</td>
<td>113</td>
<td>-1.65</td>
<td>0.330</td>
<td>0.061</td>
</tr>
<tr>
<td>Average</td>
<td>116</td>
<td>-1.55</td>
<td>0.334</td>
<td>0.059</td>
</tr>
<tr>
<td>Cu:NiO/P1</td>
<td>122</td>
<td>-1.27</td>
<td>0.314</td>
<td>0.048</td>
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<tr>
<td>Cu:NiO/P1</td>
<td>86</td>
<td>-1.04</td>
<td>0.346</td>
<td>0.029</td>
</tr>
<tr>
<td>Cu:NiO/P1</td>
<td>100</td>
<td>-1.18</td>
<td>0.336</td>
<td>0.040</td>
</tr>
<tr>
<td>Cu:NiO/P1</td>
<td>88</td>
<td>-0.83</td>
<td>0.334</td>
<td>0.025</td>
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<tr>
<td>Average</td>
<td>99</td>
<td>-1.08</td>
<td>0.332</td>
<td>0.036</td>
</tr>
</tbody>
</table>

V_{OC}: open-circuit voltage; J_{SC}: short circuit current density.

**Figure 7.** UV-vis spectra of NiO with different layer thickness with solid line and without dash line P1 dye (a); Photocurrent density at -0.3 V and -0.5 V vs. Ag/AgCl of the different NiO/P1 samples in 0.1 M PBS at pH = 7 with 0.05 M K\(_2\)S\(_2\)O\(_8\) as the electron scavenger (b).
Table 3. DSSC performance of NiO/P1 with different thickness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{OC}$ mV</th>
<th>$J_{SC}$ mA cm$^{-2}$</th>
<th>Fill factor</th>
<th>Power-to-current efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO 1/P1</td>
<td>93</td>
<td>-1.39</td>
<td>0.34</td>
<td>0.044</td>
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<tr>
<td>NiO 4 a/P1</td>
<td>88</td>
<td>-0.72</td>
<td>0.35</td>
<td>0.022</td>
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<tr>
<td>NiO 4 b/P1</td>
<td>105</td>
<td>-0.69</td>
<td>0.35</td>
<td>0.026</td>
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<td>NiO 5 a/P1</td>
<td>105</td>
<td>-0.21</td>
<td>0.34</td>
<td>0.008</td>
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<tr>
<td>NiO 5 b/P1</td>
<td>101</td>
<td>-0.21</td>
<td>0.33</td>
<td>0.007</td>
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</tbody>
</table>
Supporting Information

**Figure S1.** Photoelectrochemical performance of NiO/P1 and Cu:NiO/P1 photocathodes with various mol% Cu-doping in 0.1 M phosphate buffer at pH 7.

Fig S1 shows the photoelectrochemical performance of NiO/P1 and Cu:NiO/P1 photocathodes as function of Cu-doping percentage, demonstrating that 9 mol% doping leads to an optimum in photocurrent enhancement.

**Figure S2.** EDS analysis of 9 mol% Cu: NiO layers on FTO glass.
Figure S3. Cu 2p XPS spectra of 9 mol% Cu:NiO layer. The peaks at 932.4 eV and 952.1 eV are assigned to Cu\(^{+}\) and the peaks at 933.9 eV and 953.6 eV correspond to Cu\(^{2+}\).\(^{66,67}\) There are three characteristic satellite peaks related to Cu\(^{2+}\) ions.\(^{68}\)

Energy-dispersive X-ray spectroscopy analysis EDS, Fig. S2 confirms that the Cu percentage in the film of \(~8.2\) mol\% is quite close to the 9 mol\% in the precursor solution. X-ray photoelectron spectroscopy XPS, Fig. S3 indicates a Cu doping percentage of ca. 8.1 mol\%, in agreement with EDS analysis. Furthermore, the XPS data show that Cu\(^{+}\) and Cu\(^{2+}\) ions coexist in the film.

Figure S4. XRD patterns of NiO and Cu:NiO layers with various mol\% Cu-doping, the broad band at 2\(\theta\) = 20-30\(^{\circ}\) is due to the glass substrate.
Figure S5. Fits to the XRD patterns for a NiO; b 9 mol% Cu: NiO layers.

Fig. S4 presents the XRD patterns for all samples, showing only two peaks around 37° and 47°, which correspond to the (111) and (200) facets of cubic NiO according to XRD JCPDS card no. PDF#47-1049. Upon doping with Cu, the two peaks become broader and less intense, especially the 111 peak. Fig. S5 and Table S1 show fits to the XRD patterns and calculations of the crystallite size and d-spacing according to the Scherrer equation 1 and Bragg’s law 2:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  
\[ d = \frac{n\lambda}{2\sin \theta} \]

D presents the crystallite size, K the Scherrer constant, \( \lambda \) the wavelength of the x-ray source, \( \beta \) the line broadening at full width at half maximum, d the interplanar spacing or d-spacing, \( \theta \) the Bragg angle and n the order of diffraction. Since NiO has a cubic crystal structure, the lattice parameter a can be calculated from 3:

\[ \frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \]

with h, l and k the Miller indices. Cu-doping decreases the crystallite size and causes an expansion of the interplanar spacing, increasing the lattice parameter Table S1.
Table S1. Crystalline size and d-spacing from fits to the XRD patterns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak position 2θ °</th>
<th>FWHM °</th>
<th>Crystallite size D nm</th>
<th>d-spacing Å</th>
<th>lattice parameter Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>37.301</td>
<td>0.724</td>
<td>11.901</td>
<td>2.409</td>
<td>4.172</td>
</tr>
<tr>
<td></td>
<td>43.339</td>
<td>1.214</td>
<td>8.181</td>
<td>2.086</td>
<td></td>
</tr>
<tr>
<td>9 mol% Cu:NiO</td>
<td>37.219</td>
<td>1.105</td>
<td>8.103</td>
<td>2.414</td>
<td>4.181</td>
</tr>
<tr>
<td></td>
<td>43.282</td>
<td>1.508</td>
<td>6.887</td>
<td>2.089</td>
<td></td>
</tr>
</tbody>
</table>

Figure S6. UV-Vis absorbance spectra of NiO and Cu:NiO layers with and without P1 dye, with the Cu-doping percentage ranging between 0 mol% and 11 mol%.

Fig. S6 presents the UV-Vis absorbance A as function of wavelength of the layers with and without the P1 dye. The P1 absorbance is estimated from the difference in UV-Vis absorbance between samples with and without P1. The fraction of absorbed light $F_A$ is obtained from 4:

$$ F_A = 1 - 10^{-A} $$
Figure S7. Fraction of absorbed light of NiO/P1 and Cu: NiO/P1 layers as function of wavelength.

Fig. S7 presents $F_A$ of the P1 dye for NiO-sensitized layers with different Cu-doping percentage. The value for $F_A$ increases with Cu-doping, likely due to a smaller crystallite size Table S1 and larger surface area see main text. Fig. S8 shows a Tauc plot for the bare NiO and Cu: NiO layers.

Figure S8. Tauc plot for the UV-Vis absorbance spectra of NiO and 9 mol% Cu: NiO.
Fig. S9 presents an analysis of the relative electrochemical active area ECSA of NiO and 9 mol% Cu: NiO electrodes, with the potential window recorded in a non-Faradaic CV region in 0.1 M phosphate buffer solution (PBS) at pH = 7. The slope of the linear fits corresponds to the double layer capacitance per geometric surface area. The double layer capacitance $C_{dl}$ of Cu doped NiO and NiO are 1.8 mF/cm$^2$ and 2.1 mF/cm$^2$, respectively. This indicates a ca. 1.16 times higher ECSA for 9 mol% Cu: NiO electrodes, explaining the higher dye absorption observed in Fig. 2.
Figure S10. Photoelectrochemical performance of NiO, NiO/P1, 9 mol% Cu:NiO and 9 mol% Cu:NiO/P1 layers in 0.1 M phosphate buffer solution PBS at pH = 7. The light intensity is 1 sun AM 1.5G, > 400 nm. Prior to the measurements, the solution was degassed by N₂ for at least 20 min.

Fig. S10 presents the photoelectrochemical performance with chopped illumination with 1 sun AM 1.5G, >400 nm of bare NiO and 9 mol% Cu:NiO photocathodes and the layers photosensitized with P1 dye in 0.1 M phosphate buffer solution at pH = 7. The performance of the P1-sensitized layers largely exceeds that of layers without dye, demonstrating that P1 photoexcitation is responsible for the photocathode performance. Fig. S11 shows the cyclic voltammograms of the bare films. It is obvious that after Cu doping there is a pair of redox peaks, which corresponds to a change from Cu^{2+} to Cu^{+} or vice versa.
Figure S11. Cyclic voltammograms of bare NiO and 9 mol% Cu:NiO in 0.1 M phosphate buffer solution, recorded at a scan rate of 5 mV/s.

Figure S12. a UV-Vis absorbance spectra of fresh NiO and 9 mol% Cu:NiO layers with solid line and without dash line P1 dye, and NiO/P1 and 9 mol% Cu:NiO/P1 after I-t experiments semi-transparent line; b Photoelectrochemical performance of fresh NiO/P1 and 9 mol% Cu:NiO/P1 photocathodes and after I-t experiments.

Fig. S12 shows the UV-Vis absorbance and photoelectrochemical performance of the samples after long-time I-t experiments under 0.31 V vs. RHE applied potential. Both the UV-Vis absorbance and photoelectrochemical performance show a decrease compared with the newly prepared samples. For the 9 mol% Cu:NiO/P1 photocathode after the I-t experiment, the visible light absorbance is lower than for the newly prepared NiO/P1 photocathode, but the photocurrent is still higher, which implies the higher light absorption is not the reason for the Cu-doping induced enhancement in photocurrent.
Figure S13. Kinetic traces at 536 nm and 567 nm for 9 mol% Cu:NiO/P1. Note that Cu-doping leads to a minor red-shift in transient absorption spectra.

Fig. S14. Species associated spectra corresponding to $t_1$- $t_4$ see main text obtained from the photophysical fit of the TA data of a NiO/P1 and b 9 mol% Cu:NiO/P1 photocathodes, with Cu-doping causing a minor red-shift.

Fig. S13 presents the transient absorption kinetic traces at 536 nm and 567 nm for 9 mol% Cu:NiO/P1 layers. The vanishing difference in time between the two traces indicates hole injection to be finalized in a few ps, in addition to that hole injection also takes place within the instrumental response time of 100-150 fs see main text. Fig. S14 shows the species associated spectra corresponding to the lifetimes $t_1$-$t_4$ Table 1 obtained from target analysis of the transient absorption data using the photophysical model shown in Fig. 5. Fig. S15 shows the open circuit voltage decay in time for NiO and Cu:NiO. NiO shows a slower decay, indicative of good charge storage ability. However, in dye-sensitized
NiO hole storage at the NiO surface will promote recombination after hole injection from dye to NiO. This can also explain why Cu: NiO/P1 shows slower charge recombination.

Figure S15. Open circuit voltage $V_{oc}$ decay in time for NiO and Cu: NiO layers.

References


33. Qin, P.; Zhu, H.; Edvinsson, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. Design of an organic


Unraveling the Mechanisms of Beneficial Cu-Doping of NiO-Based Photocathodes


CHAPTER 4

Dual Role of Surface Hydroxyl Groups in the Photodynamics and Performance of NiO-based Photocathodes

Photoelectrochemical PEC cells, containing photocathodes based on functionalized NiO, show promising solar-to-hydrogen conversion efficiency. Here, we present mechanistic understanding of the photoinduced charge transfer processes occurring at the photocathode/electrolyte interface. We demonstrate by advanced photophysical characterization that surface hydroxyl groups formed at the NiO/water interface not only promote photoinduced hole transfer from the dye into the NiO, but also enhance the rate of charge recombination. Both processes are significantly slower when the photocathode is exposed to dry acetonitrile, while in air intermediate behavior is observed. These data suggest that highly efficient devices can be developed by balancing the quantity of surface hydroxyl groups of NiO, and presumably of other p-type metal oxide semiconductors.
4.1 Introduction

Development of highly efficient solar cells and photoelectrochemical (PEC) cells is essential to facilitate the energy transition and mitigate climate change. Previous research efforts to improve the performance of solar cells or PEC cells include doping of metal oxide semiconductors,\textsuperscript{1-3} evaluation of combinations of light absorbers and catalysts,\textsuperscript{4-6} and the introduction of hole or electron transport layers\textsuperscript{7-9} or surface passivation layers\textsuperscript{10-11}. However, the efficiency of in particular PEC cells is still unsatisfactory, especially the realization of effective dye-sensitized photocathodes remains a challenge.\textsuperscript{12-15} Dye-sensitized photocathodes consist of dye molecules and catalysts adsorbed on a p-type metal oxide semiconductor. The dye absorbs the light and generates the electrons and holes. Different from electrodes based on a metal oxide semiconductor only, in which light absorption and charge separation occur in the same material, the light-induced charge separation in a dye-sensitized photocathode occurs by hole injection from the dye into the semiconductor followed by electron transfer to the catalyst.

A major challenge in both types of photoelectrodes is the prevention of fast charge recombination processes leading to major efficiency losses.\textsuperscript{16-18} While the surface structure of the metal oxide is thought to play an important role in determination of the charge separation efficiency, mechanistic understanding is limited, and in particular the role of (surface adsorbed) water and hydroxyl groups is unclear. Li et.al. and Luo et.al. reported that surface-bound OH species on hematite (Fe$_2$O$_3$) used in PEC cells serve as a hole collection and transfer mediator, accelerating charge collection and enhancing the photocurrent.\textsuperscript{19,20} In contrast, Iandolo et.al\textsuperscript{21} concluded that an OH-terminated hematite surface acts as hole recombination center and Jiang et.al. and Li et.al. claimed that the surface hydroxyl groups on TiO$_2$ function as charge recombination centers.\textsuperscript{22,23}

Inconsistent results on the role of a hydrated semiconductor surfaces are not only observed in solar water splitting, but also in research on dye-sensitized solar cells (DSSCs). The performance of the most popular p-type semiconductor, NiO, is known to be highly sensitive to sometimes only minor differences in preparation method.\textsuperscript{24} Surface states associated with hydroxyl groups and oxygen sites of the NiO may introduce intra-bandgap states and cause charge recombination.\textsuperscript{25} Therefore, passivation of surface states seems a promising method to reduce charge recombination. Cahoon et.al applied target atomic deposition of Al on NiO and observed an improvement in solar cell efficiency in aqueous electrolyte.\textsuperscript{26} However, when investigating the performance in dry acetonitrile for comparison, the passivated NiO showed the lowest short-circuit current and efficiency. Tian et.al. reported similar results, the solar cell (in an acetonitrile electrolyte) showed a surprisingly low short-circuit current after passivating 72% of the surface states by atomic layer deposition of Al$_2$O$_3$, which was assigned to inefficient dye regeneration.\textsuperscript{27}

The surface of NiO is known to be highly complex.\textsuperscript{28-30} Surface adsorbates such as O$_2$ will promote H$_2$O adsorption and dissociation on the NiO surface, either at a defect site or at a regular site,
depending on the facet.\textsuperscript{31-34} The work function of NiO is known to linearly drop with the coverage of water molecules.\textsuperscript{35} The conductivity of NiO films has recently been reported to be determined by surface states rather than by bulk properties. \textsuperscript{27} Furthermore, the conductivity of NiO films changes dramatically after aging in natural atmosphere.\textsuperscript{36} A possible reason is a surface change due to different coverage by H\textsubscript{2}O and Ni-OH. In addition, NiO has different surface conditions in aqueous and aprotic electrolyte.\textsuperscript{37}

Considering the high surface sensitivity of NiO, the photoinduced interfacial charge carrier dynamics of a NiO-based DSSC, PEC cells or other devices likely vary in different electrolytes. However, most modern characterization techniques are not in-situ, and the characterized surface condition is hence not the same as in working conditions. In this work, we unravel for the first time the role of surface hydroxyl groups in the interfacial charge dynamics of photosensitized nanoporous NiO by time-resolved photoluminescence and femtosecond transient absorption spectroscopy under in-situ conditions. The NiO is functionalized with P1 4-bis-4-5-2,2-dicyano-vinyl-thiophene-2-yl-phenyl-amino-benzoic acid. dye molecules, which absorb well below 600 nm. Sun and co-workers designed this dye for the photosensitization of NiO and other p-type semiconductors.\textsuperscript{38} P1 is equipped with a COOH anchoring group and has a delocalized highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO) localized far away from the anchoring group, which supports light-induced charge separation. We observe that photoinduced hole injection from the P1 dye into NiO is very slow in dry acetonitrile (the surface containing small amounts of surface H\textsubscript{2}O and Ni-OH), but ultrafast in phosphate buffer solution (PBS, pH 7, i.e. ample surface H\textsubscript{2}O and Ni-OH). On the contrary, the reduced dye formed by photoinduced hole injection into the NiO decays much slower in dry acetonitrile compared with the photoelectrode in air and especially in PBS due to slower charge recombination. We demonstrate that these effects are due to a dual function of surface hydroxyl groups: increasing the hole injection rate from dye into NiO, but also promotion of hole accumulation, and thereby increasing the charge recombination rate. This work emphasizes the importance of balancing the amount of surface hydroxyl groups of NiO-based photocathodes, which likely explains the contradictory results reported in earlier publications.

4.2 Experimental Section

4.2.1 Sample Preparation

The nanoporous NiO films were prepared following a procedure reported in the chapter 3, in air with a relative humidity of 40\% to 50\%. The as-prepared NiO films were dipped into P1 dye (4-(bis-4-(5-(2,2-dicyano-vinyl)-thiophene-2-yl)-phenyl-amino)-benzoic acid, purchased from Dyenamo, Sweden) dissolved in ethanol (Supelco, >99.9 \%) for around 16 h. ZrO\textsubscript{2} films were also prepared according to an earlier reported procedure.\textsuperscript{2} The zirconium precursor solution was prepared by adding 40 mM
zirconium butoxide (Sigma-Aldrich, 80 wt. % in 1-butanol) into 1-butanol solution (Sigma-Aldrich, 99.9%). The as-prepared photoelectrodes were dipped into the precursor solution and kept at 70 °C for different times (15 min. for thin ZrO₂ and 1 hour for thick ZrO₂). Before P1 dye deposition, the layers were annealed at 475 °C for 30 min in air.

The Ni(OH)₂ layers were prepared by a chemical bath deposition method. The precursor solution was prepared by dissolving 0.03 M Ni(NO₃)₂•6H₂O (Sigma-Aldrich, 99.999%), 0.08 M urea (Sigma-Aldrich, >99%) and 0.3 M ethanolamine (Sigma-Aldrich, >99%) into Milli-Q water. The as-prepared film electrode was put into the solution and kept there at 90 °C for 10 min. Finally, the film was taken out and rinsed by Milli-Q water.

4.2.2 Characterization

The crystal structures were characterized by X-ray diffraction (Bruker D2, Cu Kα source). The UV-vis spectra were measured in transmission mode using a ThermoSci EVO600 spectrometer. The valence states of the surface were characterized by X-ray Photoelectron Spectroscopy (XPS, PHI Quantera SXM).

4.2.3 Time resolved photoluminescence spectroscopy (TRPL)

The time-resolved photoluminescence was measured by a streak camera setup (Hamamatsu, C10910), using the attenuated output of a Fianium laser (FP-532-1-s, center wavelength 532 nm, pulse duration of 300 fs, 80.37 MHz repetition rate), which was focused using a quartz lens with 50 mm focal length onto the samples in a quartz cuvette (Hellma, 10 mm optical path length) filled with air, 0.1 M phosphate buffer solution (PBS, pH=7) or anhydrous acetonitrile (Sigma-Aldrich, 99.8 %). The photoluminescence was collected using two 2-inch diameter 50 mm focal length glass lenses and focused on the input of a spectrograph (Acton SP2300, Princeton Instruments, slit width set at 100 mm) using a grating with 50 lines/mm blazed at 600 nm. The output of the spectrograph was sent to the photocathode of the streak camera. Quartz (Uqg optics) was used as the substrate to avoid background photoluminescence signal. Before each series of experiments, the spectral calibration was checked using a Hg/Ar calibration lamp (Oriel, LSP035) and adapted if necessary.

4.2.4 Femtosecond transient absorption spectroscopy (fs TA)

The fs TA setup was described in detail in chapter 2 and 3. The 800 nm pulses at 5 kHz repetition rate with a pulse duration of 35 ± 1 fs FWHM were generated by a Ti:Sapphire amplifier (Coherent, Legend Elite). A 90:10 beam splitter was used to split the 800 nm output into two beams. The 500 nm pump beam was generated by sending the major part of the 800 nm beam into an optical parametric amplifier (Coherent, Opera). The remaining part of the 800 nm beam was sent through a mechanical delay stage and after further attenuation focused into a CaF₂ crystal (Newlight Photonics, 3 mm thickness) mounted on a continuously moving stage. An OD 3 near-IR filter (NENIR30B) and OD 1 near-IR filter (NENIR10B) from Thorlabs instead of the 700 nm short-pass filters were used to extend
Chapter 4

the probe window from 700 nm to 850 nm. The polarizations of the pump and probe beams were set at 54.7° magic angle. The differential absorbance between pump on and off was obtained by chopping the pump beam at 2.5 kHz. The time resolution is ca. 100–150 fs. The samples were mounted on a continuously moving stage with a velocity of ca. 1 mm/s to refresh the measurement area regularly and avoid potential charge accumulation and photodegradation. Samples were checked for photodegradation by comparing UV–vis absorbance spectra before and after the TA measurements and no changes were observed. The pump power was kept relatively low ($<5 \times 10^{14}$ photons/(cm² pulse)) and verified to be in the linear regime. The TA experiments were carried out on the dry film in a quartz cuvette (Hellma, 5 mm optical path length) in air, PBS, and dry acetonitrile. Before the measurements, the film and cuvette were blown by N₂. To avoid sample variation, all comparative experiments were performed on the same NiO photocathode.

4.2.5 Photoelectrochemical measurements

Photoelectrochemical (PEC) properties were measured in a three-electrode cell using an VersaSTAT 3 Potentiostat under illumination by a solar simulator with AM 1.5G filter (Newport, 1 sun intensity) and a filter cutting off UV below 400 nm. An Ag/AgCl electrode and gold wire were used as the reference electrode and counter electrode. The PBS electrolyte was degassed by N₂ for more than 20 min. prior to the measurements. Scans were performed from high to low potential, with a scan rate of 5 mV/s.

4.3 Results and Discussion

4.3.1 Photoelectrode characterization

Figure 1. XPS spectra of the NiO film and deconvolution: O 1s (a) and Ni 2p₃/₂ (b) bands.

Nanoporous NiO films with a thickness of ca. 230 nm (see Fig. S1 of the supporting information for scanning electron micrographs) were prepared as described in the experimental section. The X-ray Photoelectron Spectroscopy (XPS) results are shown in Fig. 1. X-ray diffraction data of the bare NiO
layers and UV-vis absorbance spectra of bare and P1-photosensitized NiO layers are provided in Fig. S2 of the supporting information. Deconvolution of the XPS O 1s spectrum (Fig. 1a) confirms three different O species for the NiO surface. The bands at around 529.3 eV, 531.0 eV and 532.9 eV are assigned to O\(^2\), Ni-OH and surface-adsorbed H\(_2\)O, respectively.\(^{39-40}\) The ratio of O\(^2\) to OH\(^-\) surface termination is around 2:1. The assignment of the Ni 2p\(_{3/2}\) peak Fig. 1b. is non-trivial, due to the complexity of the 2p spectra.\(^41\) Here, we only assigned the peak around 853.8 eV to Ni\(^{2+}\), since the peak around 855.7 eV is likely a mixture of Ni\(^{2+}\) and Ni\(^{3+}\), as in Ni(OH)\(_2\) and NiOOH.\(^{39,42-43}\) The lack of a peak at low binding energy around 851.9 eV indicates the absence of metallic Ni in the film.\(^42\) Apparently, the surface of as-prepared NiO contains a large amount of surface hydroxyl groups, even in the high vacuum conditions required for XPS analysis.

4.3.2 Surface hydroxyl groups assist photoinduced hole injection

Figure 2. Normalized photoluminescence decay at 670 nm of the P1-sensitized layers recorded at 532 nm excitation. (a) Experimental conditions on the photoluminescence decay in the absence of NiO, while in the presence of NiO (b) the experimental conditions alter the decay. Note that in one sample the light absorption layer was terminated by a Ni(OH)\(_2\) layer, to consolidate the effect of surface OH\(^-\) groups.

Time-resolved photoluminescence PL measurements at 532 nm excitation were carried out to study the excited state dynamics of the P1 dye used for photosensitization on various substrates in different environments. Fig. 2a shows the normalized photoluminescence decay at 670 nm of P1 on quartz and on ZrO\(_2\) in air and in phosphate buffer solution (PBS, pH 7, the commonly used electrolyte for photoelectrochemical H\(_2\) evolution). All exhibit the same PL decay, showing no additional quenching channel by either photoinduced hole injection into the ZrO\(_2\) or electron injection into the PBS. Conversely, the PL decay is extremely fast for P1 on NiO (Fig. 2b), likely due to photoinduced hole injection from P1 into NiO usually occurring in less than 10 ps.\(^{44}\) When a ZrO\(_2\) layer is introduced
between the NiO surface and the P1 dye, the PL decay changes. Since ZrO\textsubscript{2} is an insulator and has a deeper valence band position than NiO and P1,\textsuperscript{45,46} it likely inhibits (part of) the photoinduced hole injection from P1 into NiO, resulting in slower PL quenching than for NiO/P1. Interestingly, when PBS is present, the PL quenching is accelerated. As the PBS has no significant effect on either the ZrO\textsubscript{2} or the P1 dye (Fig. 2a), a likely reason is a change in the structure of the NiO surface, affecting the hole injection dynamics. In aqueous electrolyte water molecules are known to be easily adsorbed on the NiO surfaces and form Ni(OH)\textsubscript{2}.\textsuperscript{38} Therefore, it is reasonable to assume that the presence of a larger quantity of surface hydroxyl groups is the reason for the decrease in PL lifetime. An additional thin layer of Ni(OH)\textsubscript{2} was deliberately deposited on top of the ZrO\textsubscript{2}/P1 layer following literature procedures to consolidate this hypothesis.\textsuperscript{47} The PL decay of ZrO\textsubscript{2}/P1/Ni(OH)\textsubscript{2} (Fig. 2b, green line) shows indeed a faster PL decay compared to ZrO\textsubscript{2}/P1. This accelerated PL decay is almost similar to NiO/ZrO\textsubscript{2}/P1 in PBS, strongly suggesting hole injection by the excited P1 dye into Ni(OH)\textsubscript{2} is responsible for the PL quenching. A different amount of surface hydroxyl groups might be the reason for the variety in hole injection rates reported in the literature.\textsuperscript{48}

Figure 3. Transient absorption spectra after excitation at 500 nm (a-c) and kinetic traces (d-f) of NiO/P1 in dry MeCN (a, d), air with a relative humidity of 40% (b, e), and PBS (c, f). The lines indicate fits from target analysis.

To investigate the role of surface hydroxyl groups in the photodynamics in detail, femtosecond transient absorption TA studies were performed on the same sample, in the order air-PBS-dry acetonitrile MeCN (Fig. 3). Considering the difference in OH\textsuperscript{-} surface termination of NiO in aqueous and nonaqueous electrolytes\textsuperscript{37} and the equilibrium between surface-dissociated adsorbed and bulk water,\textsuperscript{31,33} it is reasonable to assume that the NiO surface in aqueous solution contains more hydroxyl groups than in air and especially in dry MeCN. Similar dynamics in PBS without and with prior N\textsubscript{2}
purging (supporting information Fig. S4) exclude a role of dissolved CO$_2$ or O$_2$. The broad negative signal is due to photoinduced ground state bleach (GSB) of the P1 dye. The P1 excited state (P1*) is known to give a strong and broad positive absorbance above 550-560 nm and a weak absorbance around 410 nm.\textsuperscript{44,49} Due to hole injection from P1* into NiO the intensity of P1* decreases, whereas the characteristic spectra of P1* arise (positive bands around 420 nm and 610 nm).\textsuperscript{44} Photoinduced hole injection is known to cause a red-shift in TA spectrum due to overlapping signals of the P1 GSB, P1*, P1* and Ni$^{3+}$/4+\textsuperscript{44,49-51} (supporting information Fig. S3). It is notable that the spectra for NiO/P1 in air and especially in PBS at early times (<1 ps) are red-shifted compared to NiO/P1 in MeCN, which can be explained by more photoinduced hole injection within the instrumental response time (IRT, 100-150 fs) in air/PBS. This can also explain the less intense negative signal for NiO/P1 in dry MeCN (Fig. 3a), which is likely caused by a stronger P1* absorbance overlapping with the GSB.

Figs. 3 d-f compare the kinetic traces at 527 nm and 560 nm of NiO/P1 in dry MeCN, air and PBS. The difference between the traces at 527 nm and 560 nm is significant and mainly caused by photoinduced hole injection. The 560 nm signal is due to both P1* absorption and GSB, while the 527 nm signal is mainly due to GSB.\textsuperscript{44,49} The decay at 560 nm is hence largely due to P1* decay by hole injection into the NiO, while the decay at 527 nm is mainly due to charge recombination following hole injection. It is important to distinguish between hole injection within the IRT and beyond, which biphasic behavior is well-known.\textsuperscript{44} The difference between the traces at 527 nm and 560 nm until a few ps is the largest in MeCN, intermediate in air and the smallest in PBS, indicating more hole injection <IRT in air and in particular in PBS. A larger amount of surface hydroxyl groups hence implies extensive ultrafast photoinduced hole injection. The small difference between the 527 nm and 560 nm traces for NiO/P1 in PBS demonstrates only minor hole injection beyond the IRT, and the decay is hence mainly caused by charge recombination. In air and in particular in dry MeCN hole injection also occurs beyond the IRT until a few ps, while charge recombination occurs simultaneously and beyond.

The difference between PBS and H$_2$O environment (data in supporting information Fig. S5) is minor, demonstrating that the effect of phosphate ions is small or even negligible and not responsible for the trends shown in Fig. 3. To obtain further evidence these differences are caused by H$_2$O induced surface hydroxyl groups, we have measured a new NiO/P1 layer in air, first with a low and then with a high relative humidity, controlled by using silica gel or a KCl saturation solution in the air filled sealed cuvette containing the NiO/P1 layer (see supporting information Fig. S6-S7). The kinetic traces at 560 nm shown in Fig. 4 clearly demonstrate different dynamics. In dry air the initial <IRT rise in negative signal is followed by a slower few ps rise, similar as in Fig. 3e. In contrast, in air with a high humidity all transient signal at 560 nm develops within the IRT, similar as in PBS or H$_2$O (Figs. 3f and S5). Fig. 4 hence independently proofs that a difference in quantity of surface hydroxyl groups is responsible for the trends shown in Fig. 3.
Figure 4. Transient absorption kinetic traces after excitation at 500 nm probed at 560 nm of NiO/P1 measured first in an air filled sealed cuvette above silica gel and then above a saturated KCl solution, including fits from target analysis.

4.3.3 Surface hydroxyl groups promote charge recombination

Figure 5. Transient absorption kinetic traces after excitation at 500 nm probed at 410 nm (a) and 813 nm (b) of NiO/P1 in air and PBS, including fits from target analysis.

The decay of the TA band from 350-420 nm previously assigned to P1* is illustrative for charge carrier recombination. Fig. 5a shows the kinetic traces at 410 nm for P1/NiO in air and PBS, the transient signals in dry MeCN are very weak (Fig. S9, likely due to the low amount of P1*). In PBS the signal seems to decay faster, suggesting faster charge recombination. P1* is known to also absorb around 610 nm. The trace at 610 nm clearly shows a slower decay in MeCN compared with in air and PBS (Fig. S8 supporting information) demonstrating slower charge recombination in MeCN, but the difference between air and PBS is not obvious, possibly due to overlap in signals. Traces in the UV and near-IR are therefore compared instead (Fig. 5b). Both the traces at 410 nm and 813 nm clearly show the fastest decay P1* decay in PBS, which could be due to 1) electron injection by P1* into the
PBS and/or 2) fast charge recombination after hole injection promoted by the abundant surface hydroxyl groups. The lower photocurrent for NiO/Ni(OH)$_2$/P1 relative to NiO/P1 (Fig. 6, both measured in PBS) demonstrates that the second scenario is most likely. A possible reason for this fast charge recombination after hole injection is hole accumulation. Transition metal hydroxyl oxides are well-known supercapacitor materials, they have the ability to store charges, either from the extra bias$^{51-53}$ or from photogenerated charges$^{47,54}$. In addition, NiO is a p-type material but suffers from a poor hole mobility, which means that after ultrafast hole injection most of the holes likely remain at, or close to the OH$^-$ terminated surface. This is in agreement with literature reporting holes to be mainly pinned at the NiO surface,$^{55}$ increasing the chance to recombine with P1$^*$. 

**Table 1.** Lifetimes of NiO/P1 in various environments from target analysis, the species associated spectra are provided in Fig. S11 of the supporting information.

<table>
<thead>
<tr>
<th>Environment</th>
<th>$\tau_1$ fs.</th>
<th>$\tau_2$ ps.</th>
<th>$\tau_3$ ps.</th>
<th>$\tau_4$ ps.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCN</td>
<td>1270±28</td>
<td>11±0.2</td>
<td>370.8±11.4</td>
<td>-</td>
</tr>
<tr>
<td>Air</td>
<td>690±12</td>
<td>5.7±0.1</td>
<td>56.1±1.4</td>
<td>$\infty$</td>
</tr>
<tr>
<td>PBS</td>
<td>Within IRT</td>
<td>2.2±0.1</td>
<td>30.6±0.4</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

To quantify effects of OH$^-$ surface termination on hole injection and charge carrier recombination and account for the overlap in TA signals, target analysis has been performed based on the discussion above. The photophysical model used is shown in Fig. S10 of the supporting information and the results are provided in Table 1. Although this model is likely a simplification of the reality, it describes the TA data well. Hole injection $\tau_1$ occurs the fastest in PBS ($<$IRT), followed by air (690±12 fs) and dry MeCN (1270±28 fs). Hole injection is typically biphasic, with the slower component occurring simultaneous to fast charge carrier recombination, combined in $\tau_2$. Finally, $\tau_3$ describes slower charge carrier recombination, which is clearly identified to be the slowest in MeCN and the fastest in PBS, while $\tau_4$ presents a minor non-decaying component.
Figure 6. (a) Photoelectrochemical performance in 0.1 M phosphate buffer solution PBS at pH = 7 with chopped illumination with 1 sun AM 1.5G, >400 nm. of NiO/P1, NiO/Ni(OH)$_2$/P1 and NiO/thin ZrO$_2$/P1 photocathodes. (b) Average and errors of the photocurrent at -0.15 V vs. Ag/AgCl of NiO/P1, NiO/Ni(OH)$_2$/P1 and NiO/ZrO$_2$/P1 photocathodes.

Now that we have unraveled the dual role of surface hydroxyl groups in the photodynamics, we will discuss the effect of surface composition on the photoelectrochemical performance. In Figure 6 we compare the photocurrent traces of (i) NiO/P1, (ii) with an OH$^-$ rich surface by introducing a thin layer of Ni(OH)$_2$ and (iii) an OH$^-$ poor surface by adding a thin ZrO$_2$ layer (Fig. 6) in between the dye and the NiO surface. The surface OH$^-$ vs. O$_2^-$ ratio for these samples has been estimated by XPS and is further detailed in Fig. S12 of the supporting information. The UV-vis absorbance spectra (Fig. S13 supporting information) show no significant differences in light adsorption by P1. In addition, the intermediate photoluminescence quenching of NiO/thin ZrO$_2$/P1 relative to NiO/P1 and P1/quartz confirms the existence of some ZrO$_2$ at the interface (Fig. S14 supporting information). NiO/thin ZrO$_2$/P1 shows the highest photocurrent, NiO/P1 intermediate behavior and NiO/Ni(OH)$_2$/P1 the lowest photocurrent. Another noteworthy photocurrent feature of NiO/Ni(OH)$_2$/P1 is the significantly lower transient photocurrent after initiating illumination. This transient photocurrent usually indicates (capacitive) charge storage. The decrease in intensity of the capacitive current, without an increase in steady state photocurrent, indicates these accumulated charges likely recombine rather than being harvested, which is another indication that OH$^-$ groups at the NiO surface promote charge recombination.
Figure 7. (a) Simplified schematic diagram of the dual role of surface hydroxyl groups; promoting both photoinduced hole injection and charge recombination. (b) Energy diagram before hole injection and c. after surface hole accumulation.

Figure 7 illustrates the dual role of surface OH\(^{-}\) groups unraveled in the present work, of which the amount has been tuned from low to high by changing the environment of the photoelectrode from dry MeCN – air – PBS, or introduction of compositional changes. A low quantity of OH\(^{-}\) groups leads to a relatively low rate of photoinduced hole transfer (the blue arrow), but also prevents significant transfer of electrons from photoactivated dye molecules, lowering the rate of charge recombination. Passivation of the NiO surface by e.g. Al, Al\(_2\)O\(_3\) or ZrO\(_2\) will reduce the amount of OH\(^{-}\), which is beneficial for the photocurrent in aqueous conditions (Fig. 6 for ZrO\(_2\)),\(^{26}\) but was previously observed to be disadvantageous for the performance of solar cells (i.e. MeCN-based electrolyte),\(^{20,21}\) suggesting that the amount of surface OH\(^{-}\) should not be too low. An aqueous electrolyte (PBS) introduces a significant quantity of surface OH\(^{-}\) groups, which promote hole transfer (indicated by the increased thickness of the blue arrow) and charge recombination indicated by the thickness of the red arrow.

NiO is known to have a poor hole mobility, while Ni(OH)\(_2\) is a good hole storage material.\(^{47,52-54}\) In PBS injected holes are likely pinned at the NiO surface due to the sluggish hole mobility,\(^{55}\) promoting charge recombination with the electrons of the reduced dye molecules. This dual role of surface hydroxyl groups can be understood by the adaptive junctions theory that Boettcher proposed for semiconductor–electrocatalyst interfaces.\(^{57,58}\) In this theory, the transition-metal hydroxide or oxyhydroxide is a redox-active ion-permeable electrocatalyst, which can form an adaptive semiconductor/electrocatalyst junction. When holes are injected into this transition-metal hydroxide
thin layer, the Fermi level shifts down to the valence band of the semiconductor due to surface hole accumulation (Fig. 7), reducing the driving force for hole injection from the P1 HOMO. A low amount of surface hydroxyl groups causes less fast hole injection and may explain the biphasic photoinduced hole injection typically observed in air\(^{44}\) and also in present work (<IRT and \(690\pm 12\) fs). More surface hydroxyl groups imply more \(E_{\text{Ni(OH)\text{a}}}\) at the initial state which can accept the holes from the dye much faster, explaining the <IRT hole injection in PBS. Considering the low hole mobility of NiO,\(^{55}\) this ultrafast hole injection will likely promote hole accumulation and shift \(E_{\text{Ni(OH)\text{a}}}\) down, resulting in a larger driving force for charge recombination in PBS. Considering the similar character of transition metal oxides and hydroxides, the dual function of surface OH\(^{-}\) groups might also explain contradictory results for TiO\(_2\), Fe\(_2\)O\(_3\) and other metal oxide photoelectrodes.\(^{19-23, 26-27}\)

Our work illustrates the importance of balancing the number of surface hydroxyl groups on an oxide semiconductor surface to control photoinduced charge separation and recombination, and to realize efficient solar fuel devices.

### 4.4 Conclusion

In summary, we provide direct evidence of a dual function of an OH\(^{-}\) terminated NiO surface. Photoinduced hole injection is accelerated by an increased quantity of Ni-OH, however, the injected holes are likely pinned at the surface due to the hole storage ability of Ni(OH)\(_2\) and the low hole mobility of bulk NiO, promoting charge recombination with electrons from the reduced dye molecules. The dependency of the hole injection and recombination rate on the working environment can explain why photoelectrodes in aqueous electrolyte show inferior performance relative to similar photoelectrodes in acetonitrile-based electrolyte. The dual function of surface OH\(^{-}\) groups could also explain conflicting results in the literature, not only for NiO but also for other metal oxide based photoelectrodes. We believe our results illustrate the importance of balancing the number of surface hydroxyl groups on an oxide semiconductor to optimize photoinduced charge separation and recombination and guide the design of efficient solar devices.
Supporting Information

Figure S1. (a) Surface and (b) cross-section scanning electron micrographs of NiO on fluorine-doped tin oxide (FTO)/glass substrates.

Figure S2. (a) XRD patterns of NiO on amorphous glass; (b) UV-vis absorbance spectra of NiO with and without P1 dye.

Fig. S1 presents the surface and cross-section electron micrographs of NiO on FTO/glass, showing a homogeneous nanoporous layer with a thickness of ca. 230 nm. Fig. S2a shows the XRD peaks of NiO around 37° and 43°, which can be assigned to (111) and (200) facets of NiO. The featureless band around 22° is due to the amorphous glass substrate. Fig. S2b shows the UV-vis absorbance spectra of NiO with and without P1 dye, with NiO/P1 showing maximum absorbance around 500 nm.
**Figure S3.** TA signals of NiO/P1 photoelectrodes, the arrows indicate the spectral evolution due to hole injection by P1* into the NiO.

Fig. S3 illustrates the overlap in TA signals of NiO/P1 photoelectrodes, with a broad ground state bleach (GSB) due to absorption by the P1 dye. Photoexcitation gives the excited state P1*, with a strong absorption around 560 nm and a weak absorption around 410 nm (in MeCN). The signal of P1* of NiO/P1 might be red-shifted due to electronic coupling. After hole injection from P1* into NiO, the formed P1•- shows absorption bands around 610 nm and 420 nm. Hammarström et. al. observed that Ni^{3+} or Ni^{4+} sites give rise to absorption >600 nm.

**Figure S4.** Kinetic traces of the same NiO/P1 layer in PBS without and with prior N\textsubscript{2} bubbling for 1 h, including fits from target analysis as solid lines.
Dual Role of Surface Hydroxyl Groups in the Photodynamics and Performance of NiO-based Photocathodes

Figure S5. Kinetic traces of the NiO/P1 layer in milli-Q H$_2$O, including fits from target analysis as solid lines.

Fig. S4 shows selected kinetic traces for the same Ni/P1 sample in PBS without and with prior N$_2$ bubbling for 1 h to remove dissolved O$_2$ and CO$_2$. The minor difference between the fits at early times is likely due to a slightly shifted P1* spectrum resulting from fitting in Glotaran for both cases. The similarity in data shows that bubbling with N$_2$ for 1 h does not alter the photodynamics, excluding a significant effect of dissolved O$_2$ or CO$_2$. The little stronger GSB relative to the P1* signal (560 nm) compared to Fig. 3f in the main text is likely due to small variations in absorbance of different samples.

Fig. S5 shows selected kinetic traces for Ni/P1 in milli-Q H$_2$O, with the only minor difference with PBS (Fig. 3 main text) excluding a significant effect of phosphate ions on the photodynamics.

Figure S6. Illustration of the transient absorption measurements in different environments.
Figure S7. Transient absorption spectra after excitation at 500 nm of NiO/P1 in (a) air dried with silica gel and (b) air in equilibrium with a KCl saturated solution. The solid lines present fits from target analysis. The deviation between fit and the data <540 nm at 250 fs is due to the chirp correction.

Fig. S6 illustrates the experimental setup used for investigating the role of air with different relative humidity on the photodynamics. Silica gel is usually used in a desiccator to keep the environment dry. KCl saturated solution can be used to control the air relative humidity to more than 80%.59 Fig. S7 presents the transient absorption spectra for these two cases including fits from target analysis (Fig. S10) as solid lines.

Figure S8. Kinetic traces at 610 nm of NiO/P1 in dry MeCN, air and PBS, including fits from target analysis as solid lines.

Fig. S8 shows the kinetic traces at 610 nm. It is obvious that NiO/P1 in dry MeCN shows a much slower decay compared with in air and PBS. The difference between air and PBS is less obvious, but clearly visible around 813 nm (Fig. 5b main text).
Figure S9. Kinetic traces at 410 nm of NiO/P1 in MeCN, including fits from target analysis as solid lines.

Fig. S9 shows the kinetic trace at 410 nm of NiO/P1 in MeCN, previously assigned to P1•− and illustrative for charge carrier recombination. The weaker signal relative to NiO/P1 in air or PBS (main text Fig. 5a) is likely caused by slower hole injection assigned to the low abundance of surface OH− groups. We therefore neglect P1•− formed during the IRT in MeCN in the model used for target analysis (Fig. S10, please see our recent publication1 for further motivation of this photophysical model). In contrast, most of hole injection takes place within the IRT for NiO/P1 in PBS. A relatively low concentration of (surface) Ni3+ and Ni4+ giving rise to signal >600 nm is observed in MeCN. The obtained species associated spectra are shown in Fig. S11 and the obtained lifetimes are presented in Table 1 of the main text.

Figure S10. Photophysical model used for target analysis of NiO/P1 in dry MeCN (left), air (middle) and PBS (right). IRT = instrumental response time (100-150 fs).
**Figure S11.** Species associated spectra (SAS) obtained from target analysis for NiO/P1 in (a) MeCN, (b) air and (c) PBS.

**Figure S12.** O 1s XPS spectra of NiO (a), NiO/ZrO$_2$ (b) and NiO/Ni(OH)$_2$ (c) and ratio of OH$^-$ vs. O$^{2-}$ on the surface (d).

Fig. S12 shows the O 1s XPS spectra of NiO (a), NiO/ZrO$_2$ (b) and NiO/Ni(OH)$_2$ (c) and the ratio of OH$^-$ vs. O$^{2-}$ on the surface (d), indicating that the quantity of surface hydroxyl group is the highest for NiO/Ni(OH)$_2$ and lowest for NiO/ZrO$_2$. 
**Figure S13.** UV-vis absorbance spectra of NiO/Ni(OH)$_2$/P1 and NiO/ZrO$_2$/P1.

Fig. S13 shows the UV-vis absorbance spectra of NiO/Ni(OH)$_2$ (a) and NiO/thin ZrO$_2$ (b) with and without P1 dye. Alike for the NiO-based electrode (Fig. S1b), also here the typical P1 absorption centered around 500 nm is observed.

**Figure S14.** Normalized photoluminescence decay at 670 nm of different samples in air.

Fig. S14 shows the PL decay in air, for quartz/P1, NiO/P1 and NiO/thin ZrO$_2$/P1. The PL signal of NiO/P1 decays very fast compared with quartz/P1 due to ultrafast hole injection (<10 ps) from P1* into the NiO. Intermediate behavior is observed for NiO/thin ZrO$_2$/P1, indicative for some hole injection.
References


52. Xie M.; Duan S.; Shen Y.; Fang K.; Wang Y.; Lin M.; Guo X. In-Situ-Grown Mg(OH)2-Derived Hybrid α-Ni(OH)2 for Highly Stable Supercapacitor. *ACS Energy Lett.* **2016**, *1*, 814-819.


Dual Role of Surface Hydroxyl Groups in the Photodynamics and Performance of NiO-based Photocathodes
In present study we investigate the effect of the external potential on a dye-sensitized NiO photocathode on the light-induced charge carrier dynamics by time-resolved photoluminescence and femtosecond transient absorption spectroscopy under operating conditions. Instead of the anticipated acceleration of photoinduced hole injection from dye into NiO at more negative applied potential, we observe that both hole injection and charge recombination are slowed down. We assign this effect to a variation in OH$^-$ ion concentration in the inner Helmholtz plane (IHP) of the electrochemical double layer with applied potential, showing that ion adsorption and desorption onto the NiO surface play an essential role as a relay in light-induced charge transfer and recombination. Our work highlights the key role of ions at the electrode surface and in the electrolyte in the realization of efficient solar to fuel devices.
5.1 Introduction

The development of an efficient dye-sensitized photoelectrochemical (DSPEC) cell can contribute to mitigating energy and environmental challenges via converting and storing solar energy into chemical bonds. However, the overall efficiency of the DSPEC cell is limited by severe charge recombination at the photocathode, which has a substantially lower performance than the photoanode. In a dye-sensitized photocathode, a monolayer of a molecular dye is anchored onto the surface of a p-type semiconductor and functions as the light absorber. A catalyst for proton or CO$_2$ reduction can be linked to the dye, co-adsorbed on the semiconductor or even dissolved into the electrolyte. Light-induced charge separation by hole injection from the dye into the valence band of the semiconductor should be followed by electron transfer to the catalyst. This working principle differs from conventional photoelectrodes, based on e.g. Fe$_2$O$_3$ or Cu$_2$O, where light absorption and charge separation take place in the same material. In this case, the external potential (positive bias for n-type and negative bias for p-type semiconductors) facilitates light-induced charge separation and retards charge recombination in the semiconductor by introducing more bend bending, leading to a higher photocurrent at more positive (photoanode) or more negative potential (photocathode). However, whether an applied potential has the same effect on DSPEC cells with their configuration based on light-induced charge separation at the dye-semiconductor interface rather than inside the semiconductor is unknown, although some dye-sensitized photocathodes show surprisingly low photocurrents at more negative bias potentials. The composition of the electrolyte may also play an important role here.

Ultrafast spectroscopy is highly useful to investigate the light-induced processes in photoactive materials. Notably, most ultrafast spectroscopy studies on dye-sensitized photocathodes have been carried out in air or in an organic solvent instead of under operating conditions. Though, some femtosecond transient absorption studies on dye-sensitized NiO photocathodes showed that a negative potential could increase the hole injection efficiency and slow down charge recombination. However, these studies were carried out in an acetonitrile-based electrolyte, while for proton or CO$_2$ reduction an aqueous electrolyte is needed. Moreover, we recently observed that the working environment of a NiO-based photocathode plays an important role in both the light-induced hole injection and charge recombination dynamics. So far, it is unknown whether, and if so how, the external bias potential affects the charge separation and recombination dynamics in an aqueous electrolyte.

In this work, we investigate the effect of external bias potential on the photodynamics of a NiO-based photocathode in phosphate buffer solution (PBS) by UV-Vis, time-resolved photoluminescence (TRPL) and femtosecond transient absorption (TA) spectroscopy. The nanostructured NiO is functionalized with a benchmark dye P1 [4-(bis-4-(5-(2,2-dicyano-vinyl)-thiophene-2-yl)-phenyl-
amino)-benzoic acid, especially designed for the functionalization of p-type semiconductors. We observed that both light-induced hole injection from P1 into the NiO and charge recombination strongly depend on the applied external potential, and assigned the trends observed to a change in ions in the inner Helmholtz plane (IHP) of the electrochemical double layer. Our work demonstrates the important role of bias dependent ion adsorption in the electrochemical double layer on the interface photodynamics during operation.

5.2 Experimental Section

5.2.1 NiO Preparation

The NiO films were prepared by a chemical bath deposition method, followed by annealing. The 0.075 M Ni(NO$_3$)$_2$•6 H$_2$O (Sigma-Aldrich, 99.999%), 0.2 M urea (Sigma-Aldrich, >99%) and 0.75 M ethanolamine (Sigma-Aldrich, >99%) precursors were sequentially dissolved into Milli-Q water. Fluorine-doped tin oxide (FTO, 2× 2.5 cm) substrates (Sigma-Aldrich, cleaned using acetone, isopropanol and ethanol) were put into the solution, and films were grown on the FTO for 3 hours at 90 °C, followed by rinsing with Milli-Q water. Finally, the NiO films were obtained by annealing at 450 °C for 1 hour in static air. The NiO films were immersed into 0.3 mM P1 dye solution (4-(bis-4-[5-(2,2-dicyano-vinyl)-thiophene-2-yl]-phenyl-amino)-benzoic acid, Dyenamo, Sweden) in ethanol (Supelco, >99.9 %).

5.2.2 ZrO$_2$ preparation

The cleaned FTO plates were treated in a UV-ozone photoreactor (UVP PR-100) for 30 min, after they were cut up in 20 × 20 mm pieces. Two sides of the plates were covered along the full length with adhesive tape (Scotch® Magic™ tape 8-1933R8), and ZrO$_2$ nanoparticle paste (Solaronix, ZT/SP Ref 46411) was applied on the top of the plate with a glass rod. The paste was then smeared from top to bottom using the edge of a glass plate, which was held at an acute angle (< 30°). This process was repeated until a homogeneous layer of the paste was obtained. The tape was removed and the plates were thermally annealed at 500 °C for 30 min (with a temperature ramp of 20 °C/min). The plates were taken out of the oven immediately after the program finished.

5.2.3 Characterization

All the in-situ experiments were carried out in a three-electrode cell with the NiO film as the working electrode, an Ag/AgCl reference electrode and a Pt wire as the counter electrode. The electrolyte used consisted of a phosphate buffer solution (PBS) with a pH value around 7. Before each experiment, the electrolyte was degassed by flowing N$_2$ for at least 30 min. The UV-Vis absorbance spectra of the films were recorded using a ThermoSci EVO600 spectrometer. The nanomorphology of the layers was studied by a Zeiss MERLIN HR-SEM. The crystal structures were characterized by X-ray diffraction (Bruker D2, Cu Kα source).
5.2.4 Time-resolved photoluminescence spectroscopy (TRPL)

The setup used for time-resolved photoluminescence has been described in detail in chapters 3 and 5. Briefly, a Fianium laser (FP-532-1-s, center wavelength 532 nm, pulse duration of 300 fs, 80.37 MHz repetition rate) was used as the light source. For experiments with UV excitation (267 nm), the laser output was focused into a 3 mm β-BaB₂O₄ crystal (Newlight Photonics). The residual 532 nm output was removed by using three dichroic mirrors (Thorlabs, MBI-K04) and a FGUV11-UV filter (Thorlabs). The sample was kept in a quartz cuvette (Hellma, 10 mm optical path length) as the working electrode in 0.1 M phosphate buffer solution (PBS, pH=7) as the electrolyte, a Pt counter electrode and an Ag/AgCl reference electrode. The applied potential was controlled by an Emstat3 potentiostat (PalmSens). The spectral calibration was checked and adapted if necessary using a Hg/Ar calibration lamp (Oriel, LSP035). The spectral sensitivity of the PL spectra was corrected by the equations below, which were determined by comparing the measured spectrum of a black body lamp (Ocean Optics, HL-2000) with the calibrated spectrum:

\[
\text{Real PL spectrum} = \frac{\text{measured PL spectrum}}{Y}
\]

\[
Y = 110 - 0.0012 \text{ (wavelength in nm} - 600)^2
\]

5.2.5 Femtosecond transient absorption spectroscopy (fs TA)

The setup used for transient absorption experiments has been described in detail in our previous chapters 2-4. To avoid a potential (verified to be minor) role of sample variation, all comparative experiments were performed on the same NiO sample.

5.3 Results and discussion

![UV-Vis spectra of NiO in PBS electrolyte (pH=7) under various negative (a) and positive (b) external potentials. The indicated potentials are vs. Ag/AgCl.](image_url)

**Figure 1.** UV-Vis spectra of NiO in PBS electrolyte (pH=7) under various negative (a) and positive (b) external potentials. The indicated potentials are vs. Ag/AgCl.
The scanning electron micrographs and x-ray diffraction patterns of the oxidized Ni on fluorine-doped tin oxide (FTO) substrates are shown in Figures S1 and S2, demonstrating NiO with a highly porous layer structure, extending out of the FTO surface by approximately 2 µm. Figure 1a shows the UV-Vis absorbance spectra of the NiO film in PBS (pH = 7, the commonly used electrolyte) at various applied negative potentials from 0 V to -0.9 V. Clearly the spectra are very similar, indicating that reduction of Ni$^{2+}$ to Ni is minor or negligible in this potential range. However, with a potential change from 0 V to +0.9 V the visible absorbance of the NiO film increases substantially (Figure 1b), initiating at ~0.3 V and becoming even more pronounced from potentials around 0.7 V. It is widely accepted that NiO may show a gray or black color due to a large amount of defects (Ni$^{3+}$). However, the oxidation potential of Ni$^{2+}$ to Ni$^{3+}$ is around 1.4 V vs. RHE (reversible hydrogen electrode, i.e. ~0.7 V vs. Ag/AgCl, see Figure S3). Therefore, the increase in visible light absorption <0.7 V in Figure 1b is not due to electrochemical oxidation of bulk NiO, which is further confirmed by the XPS results in Figure S4. Therefore, we believe that surface related hydroxylation phenomena forming different phases of Ni-OH in the IHP are responsible for the observed changes in UV-Vis spectra. The quantity of OH$^{-}$ ions in the IHP, adsorbed on the NiO surface, will increase with a more positive potential, while a negative potential will promote H$^{+}$ adsorption. Furthermore, the extraction/intercalation of H$^{+}$ and OH$^{-}$ ions from/into the NiO films can lead to electrochromic phenomena. Therefore, we assign the changes in the UV-Vis spectra with applied potential to compositional surface modifications associated with the IHP.

Figure 2. Photoluminescence intensity at 670 nm of NiO/P1 in PBS electrolyte (0.1 M, pH=7) following excitation at 532 nm as function of the applied external potential.

To elucidate the photoinduced dynamics of NiO/P1 in PBS electrolyte under various external bias potentials, the spectrotomtemporal photoluminescence (PL) behavior was measured by streak camera detection (Figure S5). As bare NiO does not show any PL in this wavelength range following excitation at 532 nm, the PL signal in Figure S5 primarily originates from the excited P1 dye (P1*). On an insulating ZrO$_2$ support, the PL lifetime of P1* equals ca. 250 ps. Light-induced hole
injection from P1* into NiO is known to occur in a few hundred fs to several ps.\textsuperscript{41} Although as a result the PL decays of P1 on NiO are within the instrumental response time of the streak camera, the PL intensity as function of applied potential shown in Figure 2 is indicative of the hole injection rate from P1* into the NiO causing PL quenching. A positive potential leads to strong PL quenching, while a negative potential has less effect, which suggests that a positive potential accelerates photoinduced hole injection. This faster hole injection can be understood by the dual function of surface-adsorbed OH\textsuperscript{-} in the IHP, which we recently observed to promote both hole injection and recombination,\textsuperscript{30} with the concentration increasing with more positive potential. Considering the dimensions of the P1 dye, we assume band bending in NiO/PBS and NiO/P1/PBS to be similar. NiO shows a very weak PL signal at 0 V to -0.8 V following excitation at 267 nm, while the PL is more intense at positive potentials (Figure S6). According to the dead layer model, the thickness of the dead layer increases with more band bending (Figure S7), leading to a lower PL intensity.\textsuperscript{42,43} Hence, the higher PL intensity of NiO at more positive potential indicates less band bending. Therefore, a significant effect of band bending in the NiO on the trend shown in Figure 2 can be excluded from the PL data obtained for NiO in PBS using 267 nm excitation. As a more positive potential implies a decrease in energy level difference between the valence band of the NiO and the HOMO of the P1 dye, this cannot explain the faster hole injection indicated by the trend in Figure 2. The opposite dependency of the PL intensity on the applied bias potential observed for ZrO\textsubscript{2}/P1 following excitation at 532 nm (Figure S8) compared to NiO/P1 (Figure 2 and S5) indicates that Stark effects and changes in the solvation shell of the P1 dye molecules do not play a significant role in the bias-dependent data of NiO/P1.

**Figure 3.** Transient absorption spectra at different time delays after excitation at 500 nm of NiO/P1 in PBS electrolyte (0.1 M, pH=7) under various external potentials (a-e) and the spectra at 250 fs (f). The solid lines indicate results from target analysis.
Femtosecond transient absorption (TA) studies were performed to further investigate the role of the external potential in the interfacial photodynamics of NiO/P1 in PBS electrolyte. Figures 3a-e show the TA spectra at various applied potentials. These data have been recorded on the same NiO/P1 sample to avoid any potential effect of sample to sample variations, although these are minor. The broad negative signal is due to the photoinduced ground state bleach (GSB) of the P1 dye. \( \text{P1}^* \) is known to give a strong and broad positive absorbance around 550–560 nm. \( \text{P1}^* \) due to hole injection from P1* into NiO, the P1* signal decreases and the characteristic absorbance around 610 nm of P1 arises, causing a red-shift in spectrum with time. The decay in signal is due to charge recombination. Hole injection from P1* into NiO is typically a biphasic process, with the fastest component within the TA instrumental response time (IRT, 100–150 fs). The early-time spectra can hence be used to assess whether the applied potential affects the extent of ultrafast hole injection within the IRT. However, the spectrum at 250 fs at +0.8 V is clearly blue-shifted and broader than the spectra at less positive potentials (Figure 3f), which seems in contradiction with the faster hole injection indicated by stronger PL quenching (Figure 2). Ni\(^{2+}\) oxidation at +0.8 V into Ni\(^{3+}/Ni^{4+}\) by the external potential/hole injection is the likely reason, which can lead to an increase in absorption above 560 nm.

**Figure 4.** Transient absorption kinetic traces at 570 nm and 660 nm after excitation at 500 nm of NiO/P1 in PBS electrolyte (0.1 M, pH=7) under various external potentials vs. Ag/AgCl (a-e). In (f) the kinetic traces at 570 nm at various applied potentials are shown. The solid lines indicate results from target analysis.

Figures 4a-e compare the TA kinetic traces at 570 nm and 660 nm at different potentials. The transient signal at 570 nm is predominantly due to P1* (positive signal), GSB (negative signal) and P1 formed due to hole injection (positive signal), while the signal at 660 nm is primarily due to P1*. When
NiO/P1 is exposed to an aqueous solution or to air with a high relative humidity, most of the hole injection occurs ultrafast and is finished within the IRT (100-150 fs), only a minor part of the hole injection occurs slower (1-2 ps). The strong PL quenching especially at +0.8 V (Figure 2) already indicates that hole injection from P1* into NiO occurs the fastest at these conditions, and becomes gradually slower on moving towards a negative applied potential, which is supported by the TA kinetic traces at 660 nm. At positive potentials the TA signal fully develops <IRT, while at negative applied potentials a minor further ~1 ps rise is observed indicating a slower hole injection component. Comparison of the transient signals at 570 nm at different potentials (Figure 4f) shows that charge recombination becomes slower with more negative potential. Retardation of charge recombination at negative potential was reported earlier and explained by filling of intra-gap trap states. However, in that study performed in acetonitrile hole injection is also accelerated by a more negative potential, in contrast to the trend shown in Figures 2 and 4. A likely reason for this contrast is a strong dependency of the NiO surface termination on the working environment. Considering the dual role of surface OH we unraveled recently, accelerating both hole injection and charge recombination, the dependency of the photodynamics on the external potential observed here is likely due to a change in ions (H+ or OH) in the IHP. The quantity of surface OH ions is the highest at positive potential, resulting in both fast photoinduced hole injection and charge recombination. This dual role of surface OH becomes gradually less when moving to negative potentials. We cautiously assign the small difference between -0.4 V and -0.8 V to a saturation in the quantity of surface-absorbed H+ in the IHP.

Figure 5. Proposed model to explain the effect of the positive and negative external potentials on the NiO/P1 interface photodynamics. IHP: inner Helmholtz plane; OHP: outer Helmholtz plane.
Figure 5 presents a model that can explain the effect of the different external potentials on the interface photodynamics of NiO/P1 in PBS observed here. At the electrode/electrolyte interface, two types of electrochemical processes can occur. One is the Faradaic process, i.e. the oxidation or reduction reaction. The second type is the non-Faradaic process, in which surface adsorption and desorption occur and the structure of the electrode/electrolyte interface changes with applied bias potential and electrolyte composition. For NiO the Faradaic process leading to Ni$^{2+}$/Ni$^{3+}$ oxidation predominantly occurs at ~1.4 V vs. RHE, i.e. ~0.7 V vs. Ag/AgCl\(^{\text{34,36}}\) (see also Figure S3 for a cyclic voltammogram of NiO in PBS), implying that at lower potential cation (H\(^{+}\)) and anion (OH\(^{-}\)) adsorption onto the NiO surface and desorption into the PBS are the dominant processes. Other ions like PO\(_4^{2-}\) or HPO\(_4^{2-}\) might also play a role, but we observed earlier that their effect on the photodynamics is insignificant compared to OH\(^{-}\), which we observed to promote both photoinduced hole injection and charge recombination.\(^{30}\) The present work clearly demonstrates that the interfacial photodynamics change with applied external potential before oxidation of Ni\(^{2+}\) into Ni\(^{3+}\) occurs. Therefore, we propose that the non-Faradaic process, i.e. ion adsorption and desorption onto the NiO surface, plays an essential role as a relay in the light-induced charge transfer and recombination processes. This effect has not gained attention yet due to the lack of ultrafast spectroscopy studies under in-situ conditions. The positively charged NiO attracts OH\(^{-}\) ions into the IHP, which become adsorbed onto the NiO surface and as a result accelerate light-induced hole injection and charge recombination. In contrast, negatively charged NiO favors H\(^{+}\) adsorption, slowing down both hole injection and charge recombination, but with less dependency on the applied potential compared to positive potential. These effects have been quantified by target analysis to account for the overlap in TA signals and include bias-dependent oxidation states in the NiO using the open source program Glotaran\(^{48}\) and the photophysical models shown in Figure S9. The species associated spectra from target analysis and a detailed explanation are given in the Supporting Information and Figure S10. Table 1 presents the obtained lifetimes, with \(\tau_1\) hole injection from P1\(^{*}\) into the IHP and \(\tau_2\) hole transfer from the IHP into the NiO. Charge recombination is assumed to occur either between P1\(^{-}\) and holes localized at the NiO surface (\(\tau_3\)) or in the NiO bulk (\(\tau_4\)). The lifetimes are the longest at -0.8 V and gradually become shorter with more positive potential. In summary, our results show that the adsorbed ions play a more important role in the photoinduced interface charge transfer dynamics than the band bending in the dye-sensitized NiO photocathode induced by the applied potential. This can explain the different results in this work (negative potential leads to slower photoinduced hole injection in aqueous solution) and in the literature (negative potential promotes hole injection in acetonitrile).\(^25\) Our work highlights the key role of ions in the IHP and at the photocathode surface, controlled by the external bias potential, in the realization of efficient solar to fuel devices.
Table 1. Time constants from target analysis of NiO/P1 in PBS electrolyte (0.1 M, pH=7) under various external potentials vs. Ag/AgCl.

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<th>Potential (V)</th>
<th>$\tau_1$ (fs)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
<th>$\tau_4$ (ps)</th>
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<td>+0.8</td>
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<tr>
<td>+0.4</td>
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<tr>
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<td>IRT</td>
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<td>63.2 ± 0.8</td>
<td>$\infty$</td>
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<tr>
<td>-0.4</td>
<td>776.2 ± 25</td>
<td>6.5 ± 0.1</td>
<td>79.0 ± 1.3</td>
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<td>-0.8</td>
<td>1115 ± 38</td>
<td>7.2 ± 0.1</td>
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</table>

5.4 Conclusion

This in-situ time-resolved photoluminescence and femtosecond transient absorption spectroscopy study uncovers a major effect of the applied external potential on the interface photodynamics of NiO-based and presumably of other p-type metal oxide semiconductor-based photocathodes in aqueous electrolyte for applications including solar water splitting and CO$_2$ reduction. We show that the main effects of the external potential likely arise from changes in surface ion adsorption in the IHP, which plays a key role as nondirectional charge transfer relay. This study opens a new research direction to explore the effect of different ions in the IHP on the photocathode photodynamics and performance.
Supporting Information

Characterization of the NiO layer on FTO

Figure S1. Surface (a) and cross-sectional (b) SEM images of NiO on the FTO substrate. The NiO film is highly porous, consisting of vertically oriented thin flakes, extending out of the substrate by approximately 2 µm.

Figure S2. XRD patterns of NiO on the FTO substrate, with the Miller indices indicated. The diffraction lines can be assigned to FTO and NiO.
Cyclic voltammetry of the NiO layer on FTO

Figure S3. Cyclic voltammogram of NiO in PBS (pH = 7) recorded with a 5 mV/s scan rate.

Figure S1 shows the surface and cross-sectional SEM images of NiO on FTO, and Figure S2 the XRD patterns of NiO on FTO, including the assignment of the diffraction lines, and the FTO substrate. Figure S3 shows the cyclic voltammogram of NiO in PBS recorded with 5 mV/s scan rate. The peak at around 0.7 V can be assigned to the Ni$^{2+}$ to Ni$^{3+}$ oxidation$^{34-36}$ and the other signals to the capacitive current. Reduction of Ni$^{3+}$ to Ni is minor or negligible in this voltage range.

Figure S4. Ni 2p XPS spectra of the NiO film immediately after applying the indicated external potential in pH = 7 PBS electrolyte.
Figure S5. Time-resolved photoluminescence decay profiles of NiO/P1 in PBS electrolyte (pH = 7) at various external potentials following excitation at 532 nm. The potential is vs. Ag/AgCl.

Figure S4 shows the Ni 2p XPS spectra of the NiO film immediately after applying different external potentials in pH = 7 PBS electrolyte. Figure S5 shows the photoluminescence decay profiles of NiO/P1 in PBS electrolyte (pH = 7) at various external potentials following excitation at 532 nm. As NiO does not show any emission in this wavelength range after 532 nm excitation, the signal in Figure S5 primarily originates from the excited P1 dye (P1*), which decays quickly due to ultrafast hole injection into the NiO. Although as a result the photoluminescence decays of P1 on NiO are within the instrumental response time of the streak camera, the photoluminescence intensity as function of applied potential shown in Figure S5 is indicative of the hole injection rate from P1* into the NiO causing PL quenching.
Photophysical Study on the Effect of the External Potential on NiO-Based Photocathodes

Figure S6. Time-resolved photoluminescence decay profiles of NiO in PBS electrolyte (pH=7) under various external potentials (vs. Ag/AgCl) after excitation at 267 nm.

Figure S7. Band bending in a p-type material under different potentials. This illustration does not include possible effects of Fermi level pinning.

Figure S6 shows the photoluminescence decays of NiO films in PBS following excitation at 267 nm at various applied potentials. The spectra at +0.8 V and +0.4 V show a higher photoluminescence intensity, which can be explained by less band bending (see schematic diagram in Figure S7). According to the dead layer model, the photoluminescence intensity relates to band bending.\textsuperscript{42,43} With more band bending, the dead layer is thicker, which results in a lower photoluminescence intensity originating from the part of the layer without band bending. NiO is a material with an indirect band gap and a defect-rich surface, resulting in a very weak photoluminescence signal. In PBS, the additional band bending caused by the NiO/electrolyte interface leads to quenching of most of the PL signal, both at 0 V and at negative potentials.
Figure S8. Time-resolved photoluminescence decay profiles of ZrO$_2$/P1 in PBS electrolyte (pH=7) under various external potentials (vs. Ag/AgCl) after excitation at 532 nm.

Figure S8 shows the PL decay profile of ZrO$_2$/P1 in PBS electrolyte under various external potentials following excitation at 532 nm. It is obvious that both the PL intensity and lifetime of P1 are quenched by the external potential, although the effects appear to be stronger at negative potential than at positive potential. Note that this trend deviates significantly from that observed for NiO/P1 (Figure 2). The PL quenching observed for P1 on the insulating ZrO$_2$ support may result from changes in the solvation shell and ZrO$_2$ surface charge.

Figure S9. Photophysical model used to describe the femtosecond transient absorption data, IRT = instrumental response time (100-150 fs), IHP = inner Helmholtz plane. The colors of the boxes correspond to the color of the species associated spectra shown in Figure S10. The grey boxes have not been included, as they decay within the IRT. The obtained time constants are presented in Table S1.
Photophysical Study on the Effect of the External Potential on NiO-Based Photocathodes

Figure S10. Species associated spectra obtained from target analysis of the TA data of NiO/P1 in PBS electrolyte (pH=7) under various external potentials vs. Ag/AgCl.

Table S1. Time constants from target analysis of NiO/P1 in PBS electrolyte (pH=7) under various external potentials vs. Ag/AgCl. IRT = instrumental response time (100-150 fs).

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>( \tau_1 ) (fs)</th>
<th>( \tau_2 ) (ps)</th>
<th>( \tau_3 ) (ps)</th>
<th>( \tau_4 ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.8</td>
<td>&lt;IRT</td>
<td>3.2 ± 0.1</td>
<td>48.2 ± 1.0</td>
<td>∞</td>
</tr>
<tr>
<td>+0.4</td>
<td>&lt;IRT</td>
<td>4.1 ± 0.1</td>
<td>51.8 ± 1.1</td>
<td>∞</td>
</tr>
<tr>
<td>0</td>
<td>&lt;IRT</td>
<td>4.7 ± 0.1</td>
<td>63.2 ± 0.8</td>
<td>∞</td>
</tr>
<tr>
<td>-0.4</td>
<td>776.2 ± 25</td>
<td>6.5 ± 0.1</td>
<td>79.0 ± 1.3</td>
<td>∞</td>
</tr>
<tr>
<td>-0.8</td>
<td>1115 ± 38</td>
<td>7.2 ± 0.1</td>
<td>78.3 ± 1.4</td>
<td>∞</td>
</tr>
</tbody>
</table>

The transient absorption data and role of the applied bias potential are well described by the photophysical model shown in Figure S9, as apparent from the fits included as solid lines in Figures 3 and 4 obtained from target analysis using the open source program Glotaran.48 A likely reason for the impact of the external bias potential observed is a strong dependency of the NiO surface termination on the working environment. Considering the dual role of surface OH\(^-\) we unraveled recently, accelerating both hole injection and charge recombination,30 the dependency of the interfacial photodynamics on the external potential is likely due to a change in ions (H\(^+\) or OH\(^-\)) in the inner Helmholtz plane (IHP). Figure S10 shows the species associated spectra from target analysis and Table S1 presents the derived time constants. At positive potentials (+0.8 V), photoinduced hole
injection from P1* into the NiO (τ₁) is assumed to occur within the instrumental response time (IRT), promoted by the abundant surface adsorbed OH. The early-time spectra are hence mainly due to P1* and the hole injected into the IHP. The hole likely localizes at a Ni³⁺ site, oxidizing it into a Ni⁴⁺ site (τ₂) causing a red-shift in spectrum and finally decays either by surface or bulk charge recombination (τ₃ and τ₄). At moderate potential (+0.4 V, 0 V) the same model still applies, but now the holes injected by P1* are assumed to localize at Ni²⁺ sites instead of Ni³⁺ sites. At negative applied potentials (-0.4 V, -0.8 V) the quantity of surface OH¿ promoting hole injection is likely very low, instead the NiO surface can be expected to be H⁺ terminated. As a result, light-induced hole injection from P1* into the IHP is slowed down to >IRT (τ₁ = 776.2 ± 25 fs at -0.4 V and 1115 ± 38 fs at -0.8 V) and the early-time spectra are mainly due to P1*. Hole injection causes a red-shift in spectrum due to the decay of P1* and formation of P1−. Holes injected into the NiO are again likely localized at Ni²⁺ sites, subsequently oxidizing them into Ni³⁺ sites (τ₂) causing a further red-shift in spectrum, and finally decaying by surface or bulk charge recombination (τ₃ and τ₄).

References

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137, 9153-9159.


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11010-11018.


The performance of dye-sensitized photoelectrochemical (DSPEC) cells is currently hampered by the low efficiency of the photocathode. Donor-acceptor (D-A) dyes for photosensitization of the p-type semiconductor have been designed to prolong light-induced charge separation by spatially separating electrons and holes. However, other potential effects of photoinduced changes on the performance have been underexposed. We have investigated the impact of photoinduced twisting of a D-A P1 dye adsorbed onto NiO on the ultrafast dynamics and photoelectrochemical performance in the absence and presence of co-adsorbed myristic acid, which has a carboxyl anchoring group and a long apolar alkyl chain. Time-resolved photoluminescence and Density Functional Theory studies show that twisting lowers the energy of the photoexcited D-A dye, while these effects are suppressed in case myristic acid is co-adsorbed on the NiO surface. The presence of myristic acid also favors light-induced charge separation, as apparent from femtosecond transient absorption, and increases the photocurrent. Very interestingly, only in the presence of myristic acid light-induced H\textsubscript{2} evolution is observed in aqueous media, despite the absence of a H\textsubscript{2} evolution catalyst. We assign the H\textsubscript{2} generation to a synergetic effect of inhibited twisting of the D-A dye radical anion increasing its electrochemical potential, combined with adsorption of H\textsuperscript{+} on the NiO surface. Our work illustrates the importance of understanding other effects of photoinduced intramolecular twisting and demonstrates that control thereof offers a simpler design approach for efficient solar fuel devices.
6.1 Introduction

Dye-sensitized photoelectrochemical cells (DSPECs) have attracted wide attention to convert solar energy into high-energy chemicals.\textsuperscript{1-4} The DSPEC consists of a photoanode performing the oxidation half reaction and a photocathode performing the reduction half reaction. Light absorption by the dye should be followed by electron transfer into the n-type semiconductor and hole transfer to the catalyst (photoanode) or hole transfer into the p-type semiconductor and electron transfer to the catalyst (photocathode). Suppression of ultrafast charge recombination is a core challenge to achieve an efficient DSPEC, with the photocathode currently limiting the performance.\textsuperscript{5-7} Strategies such as doping of the semiconductor\textsuperscript{8,9} and designing novel dyes and catalysts\textsuperscript{10-13} have therefore extensively been explored. The development of push-pull dyes with an electron donor–π bridge–electron acceptor (D-A) structure is one of the most important breakthroughs to retard charge recombination. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are usually located at different parts of the D-A structure.\textsuperscript{10, 14-15} In this way the electron and hole are spatially separated, enabling longer-lived charge separation and a higher device performance.

Due to the spatial separation of the electron and hole, the dipole moment of the dye changes after photoexcitation. To stabilize the excited molecular complex, twisting between donor and acceptor typically occurs following photoexcitation. This process results in a so-called twisted intramolecular charge transfer (TICT) state, which concept was established in 1973\textsuperscript{16} and is relatively common in D-A molecules (Figure 1).\textsuperscript{17-18} The TICT mechanism has guided the design of molecular complexes for different applications, such as sensing\textsuperscript{19} and fluorescent probes.\textsuperscript{20-21} The charge transfer or internal conversion process from the locally excited (LE) state or intramolecular charge transfer (ICT) state to the TICT state is a non-radiative process, which can quench the fluorescence of the LE/ICT state.\textsuperscript{22-23} Though D-A dyes are widely applied in dye-sensitized solar cells and photoelectrochemical cells, whether and how TICT affects the photodynamics and performance is unclear. Only a few studies focus on the impact of the TICT process on the performance, however the conclusions are contradictory. According to Ghosh and co-workers the TICT process reduces charge recombination and increases the solar cell performance.\textsuperscript{24} In contrast, Kwon et. al. reported that a twisted dye shows a 3 times lower power conversion efficiency relative to the planar analogue due to slower light-induced intramolecular charge transfer.\textsuperscript{25} As the molecular complexes were modified either by alkyl cyclization or adding an additional donor to achieve or inhibit TICT, a comparison of these results is not straightforward. The polarity of the environment can have a huge impact on molecular twisting, with a polar environment typically favoring twisting and apolar conditions inhibiting twisting.\textsuperscript{17}

In this work, a benchmark dye (4-(bis-4-(5-(2,2-dicyano-vinyl)-thiophene-2-yl)-phenyl-amino)benzoic acid, P1) designed for photosensitization of p-type semiconductors is chosen as the light absorber. The P1 dye has a carboxylic anchoring group, a triphenylamine moiety as the electron donor,
a thiophene-based bridge and an electron accepting malononitrile moiety\textsuperscript{14, 26}. The effect of enabled or inhibited TICT on the photodynamics and performance of a dye-sensitized photocathode is studied by co-adsorption of P1 and myristic acid (MA) onto nanoporous NiO. MA has the same carboxylic acid anchoring group as P1 and a long apolar alkyl chain. Time-resolved photoluminescence and Density Functional Theory studies show that TICT lowers the energy of the excited P1, while MA suppresses twisting. Very interestingly, in the presence of MA light-induced H\textsubscript{2} evolution is observed in aqueous media, despite the absence of a H\textsubscript{2} evolution catalyst. Femtosecond transient absorption (TA) experiments show major differences in the light-induced hole transfer dynamics from the D-A dye into the NiO and the charge recombination dynamics in the absence or presence of MA. These effects can be assigned to differences in NiO surface passivation. We assign the generation of H\textsubscript{2} exclusively observed in the presence of MA to a synergetic effect of inhibited twisting of the D-A dye, maintaining the electron close to the NiO surface and increasing its electrochemical potential, combined with the adsorbed H\textsuperscript{+} on the hydroxylated NiO surface. To the best of our knowledge, only the perylenemonoimide-3-hexyl substituted sexithiophene-triphenylamine (PMI-6T-TPA) dye and a Rh-ligand complex have been reported earlier to act as both light absorber and catalytic center for H\textsubscript{2} evolution and no mechanistic understanding has been reported\textsuperscript{12, 27}. We believe our work will generate interest in designing TICT-controlled dyes for highly efficient photocathodes.

![Figure 1. Potential energy diagram for photoinduced twisting of a donor-acceptor (D–A) dye.](image)
6.2 Experimental

6.2.1 Preparation of P1 sensitized NiO films

The NiO films were prepared by a chemical bath deposition method, followed by annealing. The 0.075 M Ni(NO$_3$)$_2$•6H$_2$O (Sigma-Aldrich, 99.999%), 0.2 M urea (Sigma-Aldrich, >99%) and 0.75 M ethanolamine (Sigma-Aldrich, >99%) precursors were sequentially dissolved into Milli-Q water. Cleaned fluorine-doped tin oxide (FTO) substrates purchased from Sigma-Aldrich were put into the solution, and films were grown on the FTO for 3 hours at 90 °C and washed by water. Finally, the NiO films were obtained by annealing at 450 °C for 1 hour in air. The NiO films were immersed into 0.3 mM P1 dye solution (4-(bis-4-[5-(2,2-dicyano-vinyl)-thiophene-2-yl]-phenyl-amino)-benzoic acid, Dyenamo, Sweden) in ethanol (Supelco, >99.9 %) with different concentrations of myristic acid (MA, Sigma-Aldrich, >98%, 0 mM, 3 mM, 15 mM and 40 mM) in the dark for ca. 16 hours.

6.2.2 ZrO$_2$ deposition

The cleaned FTO plates were treated in a UV-ozone photoreactor (UVP PR-100) for 30 min, after they were cut up in 20 × 20 mm pieces. Two sides of the plates were covered along the full length with adhesive tape (Scotch® Magic™ tape 8-1933R8), and ZrO$_2$ nanoparticle paste (Solaronix, ZT/SP Ref 46411) was applied on the top of the plate with a glass rod. The paste was then smeared from top to bottom using the edge of a glass plate, which was held at an acute angle (< 30°). This process was repeated until a homogeneous layer of the paste was obtained. The tape was removed and the plates were thermally annealed at 500 °C for 30 min (with a temperature ramp of 20 °C/min). The plates were taken out of the oven immediately after the program finished.

6.2.3 Characterization

X-ray diffraction (XRD, Bruker D2, Cu Kα source) and Scanning Electron Microscope (SEM, Zeiss MERLIN) were used to characterize the crystal structures, nanomorphology and thickness of the films. The UV-Vis absorbance spectra of the films were recorded using a ThermoSci EVO600 spectrometer. The light absorption efficiency ($F_A$) is calculated according to the equation, with $A$ the absorbance in optical density (OD):

$$F_A = (1 - 10^{-A}) \times 100 \%$$

6.2.4 TDDFT calculations

All calculations were performed within the AMS2022.103 software package developed by SCM.$^{28}$ The P1 ground state geometry was optimized using the CAM-B3LYP functional$^{29}$ in an all-electron triple-$\zeta$ polarized (TZP) Slater-type basis set including relativistic effects by means of the scalar zeroth order regular approximation (ZORA).$^{30}$ The water solvation environment was accounted for by the implicit conductor like screening model (COSMO)$^{31,33}$ and dispersion corrections (D3) were included...
with Becke-Johnson damping.\textsuperscript{34-36} The integration quality was improved over the default option by setting the numerical quality to ‘good’ and the SCF convergence criterium was tightened to 10e-8 Hartree/cycle. The optimized structure was verified to be a local minimum on the potential energy surface by performing a Hessian calculation (no imaginary frequencies). The excited state geometry optimization was performed within the framework of time-dependent density functional theory, using the Tamm-Dancoff approximation, at the same settings as the ground state optimization.\textsuperscript{37} Each optimization step included four excitations from the ground state, while the P1 structure was minimized on the potential energy surface of the first excited state.

6.2.5 Photoelectrochemical measurements

Photoelectrochemical (PEC) properties were measured in a three-electrode cell using an VersaSTAT 3 Potentiostat under illumination by a solar simulator with AM 1.5G filter (Newport, 1 sun intensity) and a filter cutting off UV below 400 nm. An Ag/AgCl electrode and gold wire were used as the reference electrode and counter electrode. The 0.1 M citrate-phosphate buffer electrolyte (pH around 3.8) was degassed by N\textsubscript{2} for more than 20 min. prior to the measurements. Scans were performed from high to low potential, with a scan rate of 5 mV/s.

6.3 Results and discussion

6.3.1 Nanostructure characterization and steady-state absorption spectra

![Figure 2. Surface (a) and cross-section (b) SEM images, XRD patterns of FTO and NiO/FTO and the peak assignments for NiO (c) and UV-Vis absorbance spectra of NiO before and after P1 sensitization in the absence and presence of 40 mM MA in the solution used for sensitization (d).](image)
The surface and cross-section scanning electron microscope (SEM) micrographs of NiO on FTO presented in Figures 2a and 2b show a leaf-like porous film structure with a thickness of around 1.8 μm. The X-ray diffraction (XRD) patterns of NiO/FTO and FTO shown in Figure 2c are in agreement with literature data,\textsuperscript{9} which confirms the film consists of NiO and does not have significant impurities. Figure 2d shows the UV-Vis absorbance spectra of NiO/FTO, corrected for the FTO substrate, NiO films sensitized with only P1, and with both P1 and MA. The weak absorbance of NiO in the visible is likely due to trap states,\textsuperscript{38-40} while the steep rise <380 nm is in agreement with the bandgap of 3.4-4.3 eV.\textsuperscript{41} The P1 dye is hence predominantly responsible for the visible light absorption.\textsuperscript{14, 26} Density functional theory (DFT) calculations indicate that in the equilibrium geometry, before excitation, the HOMO is mostly localized on the donor part of molecule, while the LUMO is mainly localized on the acceptor part (see also Figure 3c).\textsuperscript{14} P1 shows two absorption bands around 300-420 nm and 400-700 nm assigned to π-π* transitions.\textsuperscript{42} A broadening and red-shift in absorption spectra are typically observed when P1 is adsorbed on NiO, likely due to electronic coupling between P1 and NiO and deprotonation of the anchoring carboxylic acid group.\textsuperscript{12, 43} The presence of MA in the P1 solution used for NiO photosensitization lowers the absorption in the visible, likely due to competitive adsorption on the NiO surface. The surface coverage of the P1 dye on the NiO surface is reduced to about 48% and the light absorption efficiency is decreased by around 25% when MA is present (Figure S1).

6.3.2 Effect of Reduced Twisted Intramolecular Charge Transfer (TICT) on the Photodynamics

![Figure 3](image-url)  
**Figure 3.** The structure of P1 (a) and the excited state energy, ground state energy and angle changes in the excited state optimization (b). HOMO and LUMO at the optimized ground state (c) and excited state structure (d).
Figure 3a shows the two dihedral angles $\alpha$ (C-N-C-C) and $\beta$ (C-C-C-S) in the P1 structure that may change after photoexcitation. The light-induced electronic and structural processes have been calculated using time-dependent density functional theory (TDDFT). Figure 3c shows the HOMO and LUMO for the optimized ground state structure, which agree with the literature. After excitation, the TDDFT excited state optimization shows that the P1 molecule undergoes a structural change, $\alpha$ changes from -43.5° to -49.3° while $\beta$ changes from 22.9° to -19.8° (Figure 3a,b). After this twisting, the HOMO and LUMO have changed (Figure 3d), resulting in a 0.61 eV decrease in excitation energy associated with the HOMO-LUMO transition, while the excited state energy decreases by around 0.36 eV with respect to the Franck-Condon point (Figure 3b and Table S1). Interestingly, the extent of charge separation right after excitation is reduced by the twisting, since the HOMO moves towards the acceptor part of the P1 dye. Nevertheless, the oscillator strength for the excitation corresponding to the HOMO-LUMO ($S_1$) transition for the twisted dye is lower than for the non-twisted dye.

![Figure 4](image-url)

**Figure 4.** Steady-state photoluminescence spectra of ZrO$_2$/P1 and ZrO$_2$/P1-MA recorded by 532 nm excitation in air, detected using a 580 nm long-pass filter to remove residual excitation light.

As the photoluminescence (PL) from the TICT state can be expected to be red-shifted compared with the LE/ICT state (Figure 1 and DFT calculations discussed above), light-induced P1 twisting in the absence and presence of co-adsorbed MA has been studied by PL spectroscopy. The steady-state PL spectra of NiO/P1 and NiO/P1-MA are similar (Figure S2), likely due to fast hole injection from the excited P1 dye (P1*) into the NiO (typically biphasic, either in <100-150 fs or in 1-20 ps) before twisting. Hole injection causes PL quenching of the P1* LE/ICT state into the non-emitting P1 radical anion (P1•-). The similar spectra in the absence and presence of MA of the P1* LE/ICT state exclude an environmental effect on the PL. To investigate the impact of co-adsorbed MA on the TICT process, ZrO$_2$ is therefore used instead of NiO. The steady-state PL spectra shown in Figure 4 demonstrate a ca.
Limitation of molecular twisting: Upgrading a donor-acceptor dye to drive H\textsubscript{2} evolution

0.09 eV blue-shift for ZrO\textsubscript{2}/P1-MA relative to ZrO\textsubscript{2}/P1, indicating that co-adsorbed MA suppresses twisting. Furthermore, the PL intensity of ZrO\textsubscript{2}/P1-MA exceeds that of ZrO\textsubscript{2}/P1 by a factor of 6, despite the lower P1 loading and light absorption, in agreement with earlier studies showing that TICT reduces the PL quantum yield.\textsuperscript{45-46} The PL spectra of ZrO\textsubscript{2}/P1 samples prepared from P1 solutions with different MA concentrations show an increase in blue-shift with MA concentration (Figure S3), providing additional evidence for a reduction in P1 twisting by MA, and suggesting a correlation between the average twisting angle and the quantity of MA molecules. The absence of a blue-shift for a Ru-dye without D-A structure (Figure S4) consolidates this interpretation. Also co-adsorbed nonanoic acid (shorter apolar alkyl chain than MA) or 2,5,8,11-tetraoxatridecan-13-oic acid (long polar instead of apolar chain) do not show the same ability to reduce twisting as MA (Figure S5).

Figure 5. Time-resolved photoluminescence spectral profiles of ZrO\textsubscript{2}/P1 (a) and ZrO\textsubscript{2}/P1-MA (b) after 532 nm excitation in air, detected using a 580 nm long-pass filter, and the corresponding decay associated spectra and corresponding lifetimes from global analysis using a parallel decay model (c, d).

The twisting process in the absence and presence of co-adsorbed MA has been further investigated by time-resolved photoluminescence (TRPL). Albeit the spectra of ZrO\textsubscript{2}/P1 (Figure 5a) are red-shifted relative to those of ZrO\textsubscript{2}/P1-MA (Figure 5b), both show a red-shift in time following excitation. The co-adsorbed MA prolongs the PL decay (Figure S6), which shows that photoinduced charge transfer from P1 to MA is unlikely. The TRPL data are well described by a parallel model (Figure S7) and the temporal profiles and fittings are shown in Figure S8. The obtained decay associated spectra (DAS)
and the corresponding lifetimes are shown in Figures 5c (ZrO$_2$/P1) and 5d (ZrO$_2$/P1-MA). Four DAS can be identified: one centered at 606 nm (only for ZrO$_2$/P1-MA), one at 630 nm (for ZrO$_2$/P1 and ZrO$_2$/P1-MA) and one at 645 nm and 670 nm (only for ZrO$_2$/P1). Considering the suppressed P1* twisting by MA, the dependency of the PL shift on the MA quantity (Figure S3) and the similar UV-Vis spectra in absence and presence of MA (Figure S1), we assign the PL bands centered at 606 nm, 630 nm, 645 nm and 670 nm to a little, two partly and a fully twisted TICT state (Figure S7). The latter two states are only observed in case MA is absent, while in that case the 606 nm band assigned to the only slightly twisted structure relative to the LE/ICT state cannot be identified any longer. Transient absorption studies indicate that (slightly, partial or full) twisting occurs in ~17 ps for ZrO$_2$/P1 and ~35 ps for ZrO$_2$/P1-MA (Figures S7 and S9), quenching fluorescence of the LE/ICT state.

**Figure 6.** Transient absorption spectra after excitation at 500 nm (a, b) and kinetic traces (c, d) of NiO/P1 (a, c) and NiO/P1-MA (b, d) in 0.1 M citrate-phosphate buffer electrolyte at pH = 3.8 (b, d); kinetic traces at 625 nm of NiO/P1 and NiO/P1-MA (e). The solid lines indicate fits from target analysis.
To unravel the effect of co-adsorbed MA on the photoinduced hole injection and recombination dynamics between NiO and P1, fs-TA experiments have been carried out. Figures 6a and 6b show the TA spectra at various time delays of NiO/P1 and NiO/P1-MA in 0.1 M pH = 3.8 citrate-phosphate buffer electrolyte after 500 nm excitation. The negative signal is due to ground state bleach of the P1 dye, P1* gives a strong absorbance band around 550-560 nm and P1• formed after hole injection absorbs around 610 nm. The red-shift with time can thus be related to the dynamics of hole injection, which process typically occurs biphasic, either within the instrumental response time of 100-150 fs or in 1-20 ps. The TA signals decay in time due to charge recombination. The spectrum of NiO/P1-MA at 250 fs, well before vibrational relaxation and twisting (Figures S7 and S12), is ca. 25 nm blue-shifted compared to that of NiO/P1 and comparable to NiO/P1 in acetonitrile, suggesting less hole injection <100-150 fs. This is supported by the gap between the kinetic traces at 527 nm and 560 nm of NiO/P1 and NiO/P1-MA (Figures 6c and 6d). As the signal at 527 nm is mainly due to ground state bleach and the signal at 560 nm also due to P1*, the larger gap for NiO/P1-MA indicates much slower hole injection. Further evidence is provided by the TRPL results shown in Figure S11. For NiO/P1 the PL quenching due to hole injection is stronger than for NiO/P1-MA, which shows weak PL beyond the instrumental time resolution of the streak camera. The slower hole injection might be caused by the hydrophobic nature of the long alkyl chain of MA, likely decreasing the quantity of surface OH- on the NiO. This interpretation is in line with our recent work in which we observed a dual role of surface OH-; slowing down both photoinduced hole injection and charge recombination. Figure 6e compares the kinetic traces at 625 nm, which signal is for NiO/P1 mainly due to P1*, while for NiO/P1-MA at early ps times also P1* is likely to contribute due to the slow hole injection. NiO/P1-MA initially shows a faster decay than NiO/P1, likely due to the P1* decay. At later times the decay for NiO/P1-MA is slower than for NiO/P1, indicating slower charge recombination and electron transfer from P1* to MA is unlikely. The photophysical models used for target analysis and the obtained species associated spectra and lifetimes are provided in Figure S12.
6.3.3 Effect of Reduced TICT on the Photoelectrochemical Performance

![Figure 7](image)

**Figure 7.** Photoelectrochemical performance in 0.1 M citrate-phosphate buffer solution at pH = 3.8 with chopped illumination with 1 sun (AM 1.5G, >400 nm) of NiO/P1 and NiO/P1-MA (a), i-t curves at -0.35 V vs. Ag/AgCl of NiO/P1 and NiO/P1-MA (b); EC-MS results of NiO/P1-MA at -0.35 V vs. Ag/AgCl (c) with Mercury LED illumination with a UV long-pass filter (>400 nm).

To evaluate how TICT affects the photoelectrochemical performance, linear sweep voltammograms have been recorded in pH = 3.8 citrate-phosphate buffer solution using chopped illumination (Figure 7a). Before the measurements, the electrolyte was degassed by N2 for more than 20 min. to remove dissolved O2 and CO2. Despite the 25% lower light absorption efficiency (Figure S1) and slower hole injection of NiO/P1-MA compared with NiO/P1 as discussed above, NiO/P1-MA shows a higher photocurrent (Figures 7a and b). The lower dark current can be explained by the reduced electrochemical surface area of NiO caused by the hydrophobic alkyl chains of MA. Very interestingly, the presence of co-adsorbed MA leads to bubble formation both on the sample and the counter electrode (Figures S13 and S14). The composition of the bubbles has been analyzed in a flow cell (flow rate 0.85 ml/min, for details see Figure S15) using Electrochemical Mass Spectrometry (EC-MS) and a 460 nm LED lamp for illumination. Due to the fast response (0.1 s) of the EC-MS system together with the low flow rate we are able to analyze the gases and volatile products. The Figure 7c
shows an increase in mass signal m/z = 2 representing H₂ when starting illumination. The signal starts to decline as the light source is shut off. In addition, the m/z=32 (O₂) signal also shows the light response indicate the O₂ reduction happens as the side reaction. No sign of CO formation from this experiment, which confirms that the bubbles consist of H₂ and the H₂ most likely originates from water splitting instead of MA decomposition because of two reasons. Firstly, anchoring of the MA onto the NiO via its carboxylic acid group causes deprotonation, and hence the only way to generate H₂ from MA is to break the -CH₂ or -CH₃ bonds. Such reaction is comparable to methane reforming to produce hydrogen, which needs a high temperature and produces CO at the same time, while CO formation is not observed here. Secondly, the slower decays of the P1* and P1•⁻ signals in the presence of MA (PL data Figure 5 and TA data Figure 6e) show that photoinduced electron transfer to MA is unlikely.

The P1 dye has extensively been studied and is generally accepted to be incapable of generating H₂ in the absence of a H₂ evolution catalyst. Only the perylenemonoimide-3-hexyl substituted sexithiophene-triphenylamine (PMI-6T-TPA) dye and a Rh-ligand complex have been reported to combine the functionalities of light absorber and catalyst, and to the best of our knowledge mechanistic understanding is lacking. To understand how H₂ is generated on the NiO/P1-MA surface, additional experiments were carried out. Photochemical experiments in the presence of 15 vol% triethanolamine (TEOA) hole scavenger to suppress charge recombination again show only bubbles for NiO/P1-MA (Figure S16 and video S1) and not for NiO/P1 (Figure S16), which rules out an effect of prolonged P1•⁻ lifetime on H₂ formation. The Ni 2p₃/2 XPS spectra demonstrate no change in Ni oxidation state before and after the experiments (Figure S17). Also, the generation of bubbles is only observed for P1-MA adsorbed on p-type semiconductors (NiO and CuGaO₂, see Figure S18 and supporting video S2), and not for P1-MA on an insulator like ZrO₂ (Figure S19). In addition, the P1 molecular structure does not have a site that can accept protons. Therefore, we cautiously attribute the H₂ generation to a synergetic effect of MA-induced inhibited twisting of the D-A dye radical anion, which increases its electrochemical potential, along with H⁺ adsorption on the hydroxylated p-type semiconductor surface. In summary, our work demonstrates that inhibiting intramolecular twisting enables to produce H₂ without the presence of an additional catalyst. This strategy of this simple design should be further explored to establish efficient dye-sensitized photocathodes.

**6.4 Conclusions**

Donor-acceptor (D-A) dyes have been designed to prolong light-induced charge separation by spatially separating electrons and holes following photoexcitation via intramolecular twisting. We show that inhibiting photoinduced twisting of a D-A dye by co-adsorption of myristic acid (MA) onto the NiO allows to produce H₂, circumventing the need for an additional catalyst typically needed for H₂ evolution. Time-resolved photoluminescence and Density Functional Theory studies show that
twisting lowers the energy of the photoexcited P1 dye. Twisting is suppressed by the presence of co-adsorbed MA, which slows down charge recombination as follows from fs transient absorption studies and increases the photocurrent. We assign the generation of H$_2$ exclusively observed in the presence of MA to a synergetic effect of inhibited twisting of the D-A dye radical anion, increasing the electrochemical potential of the electron, combined with H$^+$ adsorption on the NiO surface. Our work illustrates the importance of understanding other effects of photoinduced twisting and demonstrates that control over the degree of twisting offers a simpler design approach for efficient solar fuel devices.
Supporting Information

**Figure S1.** UV-Vis absorbance spectra (a) and light absorption efficiency ($F_A$) as function of wavelength (b) of NiO/P1 and NiO/P1-MA after subtracting the NiO signals.

**Table S1.** The ground state and excited state energy computed in the ground state and excited state optimized geometries. The ground state energy of the ground state relaxed structure is taken as reference for all the other values.

<table>
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<th>Excited state energy (eV)</th>
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<tr>
<td>Excited state optimized</td>
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<td>2.51</td>
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</table>

**Figure S2.** Steady-state photoluminescence spectra of NiO/P1 and NiO/P1-MA recorded by 532 nm excitation in air, detected using a 580 nm long-pass filter to block residual excitation light.
**Figure S3.** Steady-state photoluminescence spectra of ZrO$_2$/P1 prepared using different MA concentrations in the solution used for photosensitization.

**Figure S4.** Ru dye molecular structure (a) and steady-state photoluminescence spectra of ZrO$_2$/Ru dye with and without co-adsorbed MA (40 mM in dipping solution) (b).

Figure S3 shows the steady-state photoluminescence spectra of ZrO$_2$/P1 and ZrO$_2$/P1-MA, showing a gradual blue-shift with increasing MA quantity. Figure S4 shows the steady-state photoluminescence spectra of a Ru dye without D-π-A structure on ZrO$_2$ in the absence and presence of MA, not showing a blue-shift induced by MA alike observed for P1.
Limitation of molecular twisting: Upgrading a donor-acceptor dye to drive \( \text{H}_2 \) evolution

**Figure S5.** Steady-state photoluminescence spectra of \( \text{ZrO}_2/\text{P1} \) prepared with 40 mM NA (a) and OA (b) in the solution used for photosensitization.

Figure S5 shows the steady-state photoluminescence spectra of \( \text{ZrO}_2/\text{P1} \) prepared with 40 mM NA (a) and OA (b) present in the solution used for photosensitization. Co-adsorption of NA also induces a blue-shift, albeit less than MA, while the blue-shift due to OA is very small.

**Figure S6.** Photoluminescence decay at 606 nm (a), 630 nm (b), 645 nm (c) and 670 nm (d) of \( \text{ZrO}_2/\text{P1} \) and \( \text{ZrO}_2/\text{P1}-\text{MA} \). In all cases the sample was excited at 532 nm. The solid lines indicate fits from global analysis.
Figure S7. Photophysical models used for global analysis of the TA and TRPL data of ZrO$_2$/P1 and ZrO$_2$/P1-MA.

Figure S8. PL spectra of ZrO$_2$/P1 (a) and ZrO$_2$/P1-MA after 532 nm excitation in air. The solid lines indicate fits from global analysis. Taking the most intense spectra as time 0.

Figure S7 shows the photophysical models used for global analysis of the TA and TRPL data of ZrO$_2$/P1 and ZrO$_2$/P1-MA. The spectra and fitting results are shown in Figure S8. The data fits well by using the model in Figure S7. The evolution associated spectra (EAS) and associated time scales obtained from global analysis of the TA data are shown in Figure S9. EAS1 likely presents the LE/ICT state before vibrational relaxation occurring in ca. 2 ps, EAS2 the LE/ICT state after vibrational relaxation and EAS3 the (to some degree) twisted TICT state. We assign the PL bands centered at 606 nm, 630 nm and 665 nm to a little, partly and fully twisted TICT state, with the first only observed in presence of MA and the latter only in absence of MA. Figure S10 indicate the model fits data well.
Limitation of molecular twisting: Upgrading a donor-acceptor dye to drive $H_2$ evolution

Figure S9. Evolution associated spectra (EAS) and corresponding lifetimes of ZrO$_2$/P1 (a) and ZrO$_2$/P1-MA (b), obtained from global analysis of the TA data using a sequential model.

Figure S10. Kinetic traces at 606 nm (a), 630 nm (b), 645 nm (c) and 670 nm (d) of ZrO$_2$/P1 and ZrO$_2$/P1-MA. The solid lines indicate fits from global analysis.
Figure S11. Time-resolved fluorescence spectral decay profiles of NiO/P1 (a) and NiO/P1-MA (b) in 0.1 M citrate-phosphate buffer electrolyte (pH = 3.8), obtained using 532 nm excitation.

Figure S12. Photophysical models used for target analysis of the TA data of NiO/P1 (a) and NiO/P1-MA (b), taking into account different hole injection rates. IRT = instrumental response time (100-150 fs). Species associated spectra (SAS) and corresponding lifetimes obtained from target analysis for NiO/P1 (c) and NiO/P1-MA (d).
Limitation of molecular twisting: Upgrading a donor-acceptor dye to drive \( \text{H}_2 \) evolution

Figure S11 shows the time-resolved photoluminescence profiles of NiO/P1 and NiO/P1-MA, obtained using 532 nm excitation. Figure S12 shows the photophysical models introduced in our earlier work \(^{47}\) used for target analysis of the TA data of NiO/P1 and NiO/P1-MA and the obtained species associated spectra and corresponding lifetimes. The models assumes hole injection from P1\(^*\) into NiO to occur either within the instrumental response time (<IRT, 100-150 fs, for NiO/P1) or in several ps (for NiO/P1-MA, causing a blue-shifted TA spectrum compared to NiO/P1 at e.g. 250 fs, see Figs. 6a and 6b and main text), as the presence of MA clearly slows down hole injection as evident from the gap in signals at 527 nm and 560 nm (Figures 6c and 6d main text). Hole injection hence likely occurs prior to vibrational relaxation in ca. 2 ps (Figure S7), as also reported by Gustavsson and co-workers.\(^{43}\) Several charge recombination rates are observed, which we assigned earlier to charge recombination between P1\(^*\) and h\(^+\) trapped at the NiO surface (the fastest recombination process) or more mobile h\(^+\) capable to reach the NiO bulk (slower recombination). Also Ni\(^{2+}\), Ni\(^{3+}\) and Ni\(^{4+}\) trap states may contribute to the signal.\(^{38}\) Light-induced P1 twisting and the suppression thereof by MA may influence the TA spectrotemporal dynamics as well. The observation that after hole injection the TA spectrum of NiO/P1-MA is still blue-shifted relative to that of NiO/P1 (ca. 15 nm at 5 ps, Figures 6a and 6b main text) may suggest that P1 twisting on NiO occurs faster than on ZrO\(_2\) (Figure S9) due to charge separation with the NiO. Twisting has not been included in the modeling to avoid overfitting. Though these models are likely a simplification of the reality, they describe the TA data well.

Figure S13. I-t curves at -0.35 V vs. Ag/AgCl of NiO/P1 and NiO/P1-MA in citric acid-phosphate buffer solution (pH = 3.8) with chopped illumination with 1 sun (AM 1.5G, >400 nm) (a); the cell used (b); digital photographs of NiO/P1 and NiO/P1-MA after the measurements (c); the sample holder (d).
Figure S13 shows the i-t curves of NiO/P1 and NiO/P1-MA measured in the cell shown in Figure S13b. The generation of bubbles causes dye and possibly also MA losses (Figure S13c), as the bubbles could not easily escape (Figure S13d shows the sample holder), likely also giving rise to the spikes in photocurrent observed in the presence of MA and the decrease in photocurrent (Figure S13a). However, it is obvious that the photocurrent density for NiO/P1-MA is higher than for NiO/P1, in agreement with the linear sweep voltammetry results shown in Figure 7a in the main text. To further investigate the stability of NiO/P1-MA, the i-t curves were measured in a cell not blocking the bubbles (Figure S14), showing a stable photocurrent and without obvious dye losses even after long measurement time.

**Figure S14.** Digital photographs of NiO/P1 (a) and NiO/P1-MA (b) during the i-t measurement at -0.35 V vs. Ag/AgCl in 0.1 M citrate-phosphate buffer solution at pH = 3.8 with chopped illumination with 1 sun (AM 1.5G, >400 nm).
Figure S15. Digital photo of the home-assembled light source combined with electrochemical mass spectrometry (EC-MS) experiments.

Figure S15 shows a schematic diagram of the setup used for EC-MS experiments. The setup was stabilized by using a continuous He flow through the electrolyte. The home-designed three electrodes cell was put in the position where the sample is faced up to prevent bubble accumulation at the surface and dye losses. The electrolyte flow was kept as low as possible and the rate is around 0.85 mL/min.

Figure S16. Digital photographs of NiO/P1 (a) and NiO/P1-MA (b) in 0.1 M citrate-phosphate buffer solution (pH = 3.8) with 15 vol% triethanolamine (TEOA) hole scavenger under illumination with 1 sun (AM 1.5G, >400 nm).

Figure S16 presents digital photographs of NiO/P1 (a) and NiO/P1-MA (b) in 0.1 M citrate-phosphate buffer solution (pH = 3.8) with 15 vol% triethanolamine (TEOA) hole scavenger under illumination with 1 sun (AM 1.5G, >400 nm), clearly showing bubble generation for the latter. Figure S17 shows
the Ni 2p$_{3/2}$ XPS spectra of NiO/P1 (a, c) and NiO/P1-MA (b, d) before and after the photoelectrochemical measurement, demonstrating no significant changes in Ni oxidation states. Figure S18 presents a digital photograph of CuGaO$_2$/P1-MA (b) in 0.1 M citrate-phosphate buffer solution with 15 vol% triethanolamine (TEOA) hole scavenger under illumination with 1 sun (AM 1.5G, >400 nm), also showing bubble formation.

**Figure S17.** Ni 2p$_{3/2}$ XPS spectra of NiO/P1 (a, c) and NiO/P1-MA (b, d) before and after the photoelectrochemical measurement.
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**Figure S18.** Digital photograph of CuGaO\(_2\)/P1-MA (b) in 0.1 M citrate-phosphate buffer solution with 15 vol\% triethanolamine (TEOA) hole scavenger under illumination with 1 sun (AM 1.5G, >400 nm).

**Figure S19.** Digital photograph of ZrO\(_2\)/P1-MA (b) in 0.1 M citrate-phosphate buffer solution with 15 vol\% triethanolamine (TEOA) hole scavenger under illumination with 1 sun (AM 1.5G, >400 nm).
Video S1. NiO/P1-MA (b) in 0.1 M citrate-phosphate buffer solution (pH = 3.8) with 15 vol% triethanolamine (TEOA) hole scavenger under illumination with 1 sun (AM 1.5G, >400 nm).

Video S2. CuGaO₂/P1-MA (b) in 0.1 M citrate-phosphate buffer solution (pH = 3.8) with 15 vol% triethanolamine (TEOA) hole scavenger under illumination with 1 sun (AM 1.5G, >400 nm).

References

Limitation of molecular twisting: Upgrading a donor-acceptor dye to drive $\text{H}_2$ evolution


46. Zhou, S.; Peng, B.; Duan, Y.; Liu, K.; Ikkala, O.; Ras, R. H., Bright and Photostable


Limitation of molecular twisting: Upgrading a donor-acceptor dye to drive $H_2$ evolution
P-type metal oxides, and in particular NiO, are typically used as hole accepting layers in dye-sensitized photocathodes. Delafossites (CuMO₂) with M=B, Al, Cr or Ga have recently been proposed as attractive substitutes for NiO, with theoretically a higher hole mobility than NiO, and therefore allowing a higher efficiency when the photocathode is applied in solar to fuel devices. We have experimentally validated the photoelectrochemical performance of photocathodes consisting of nanoporous CuBO₂ (CBO) on Fluorine-doped Tin Oxide substrates, photosensitized with a light absorbing P1 dye. Femtosecond transient absorption and time-resolved photoluminescence studies show that light-induced hole injection occurs from the P1 dye into the CBO in several ps, comparable to the time constant observed for NiO-based photocathodes. Importantly, the CBO-based photocathode shows significantly slower charge recombination than the NiO-based analogue, while photoelectrochemical experiments show a 5-fold increase in photon-to-current efficiency. These results illustrate the promise of CBO as a p-type semiconductor in solar energy conversion devices.
7.1 Introduction

The development of efficient dye-sensitized electrodes is important for the conversion of solar energy into electricity or solar fuels.\textsuperscript{1-3} Although dye-sensitized photocathodes for solar fuel generation have been studied for more than a decade,\textsuperscript{4} their performance is still insufficient for applications including solar water splitting and CO\textsubscript{2} reduction.\textsuperscript{1, 5-7} An important component of dye-sensitized photocathodes is the nanoporous wide bandgap semiconductor layer, to facilitate light-induced charge (hole) transfer from the dye into the semiconductor and further into the back-contact of the electrode, typically composed of transparent Fluorine-doped Tin Oxide. Furthermore a catalyst could either be on the photoelectrode surface or be present in the electrolyte,\textsuperscript{8-10} which after electron transfer from the dye either reduces water (protons) to generate H\textsubscript{2}, or CO\textsubscript{2} to generate formate, CO, or hydrocarbons. Significant efforts have been made to design photosensitizers and catalysts to improve the efficiency of the photocathode.\textsuperscript{11-14} So called “push-pull” dyes have especially been designed to improve the charge separation efficiency,\textsuperscript{15, 16} while the chemical structure of the anchoring group has been modified to promote hole injection in the p-type semiconductor and to improve the photocathode stability.\textsuperscript{17, 18} Furthermore, dye-catalyst assemblies have been developed to improve electron transfer to the catalyst and suppress charge recombination.\textsuperscript{19,20} Nevertheless, both time-resolved spectroscopy and computational studies provide evidence that NiO,\textsuperscript{21-23} the widely used p-type semiconductor in dye-sensitized photocathodes, is the limiting factor to realize high efficiencies.\textsuperscript{1} This limitation likely arises from a combination of fast surface charge recombination and a low bulk hole mobility.\textsuperscript{24, 25}

NiO shows p-type character due to the presence of Ni\textsuperscript{3+} defects,\textsuperscript{26} while the trap states resulting from Ni\textsuperscript{3+} or Ni\textsuperscript{4+} defects have been suggested to be the reason for the fast charge recombination.\textsuperscript{27, 28} The nature of the O 2p derived valence band of NiO\textsuperscript{26} leads to hole localization and a poor hole mobility.\textsuperscript{26} Furthermore, the NiO surface is highly sensitive to the presence of water causing surface hole accumulation. Combined with the sluggish hole conductivity in the NiO bulk, this promotes fast charge recombination.\textsuperscript{21,29,30} In addition, the valence band position of NiO is rather high, which limits the maximum output photovoltage.\textsuperscript{31} Therefore, it is crucial to find an alternative p-type semiconductor with high optical transparency, chemical stability, suitable valence band position and a high hole mobility.

In the quest for suitable alternative p-type semiconductor materials, delafossites (CuMO\textsubscript{2}, with M=B, Al, Cr, Ga,…) have been proposed to be promising alternatives for NiO.\textsuperscript{31-34} The hybridization of Cu 3d orbitals with O 2p orbitals likely promotes the hole delocalization and conductivity.\textsuperscript{35-37} According to theoretical studies, a decrease in ionic radius of the M site leads to a larger bandgap and higher conductivity of CuMO\textsubscript{2},\textsuperscript{38, 39} suggesting that especially CuBO\textsubscript{2} (CBO) is promising. Research on p-type semiconductor materials has been reviewed previously.\textsuperscript{34, 40, 41} Importantly, CBO shows a 10 times higher hole mobility than other CuMO\textsubscript{2} analogues and NiO, combined with a deeper valence
band position.\textsuperscript{39} Therefore, CBO is theoretically the best among the reported CuMO\textsubscript{2} candidates to replace NiO. However, to the best of our knowledge, this material has hardly been studied experimentally; only one paper reports the use of CBO in a dye-sensitized photocathode of a solar cell.\textsuperscript{42} Reproducible synthesis of CBO is challenging, while the fundamental understanding of the performance of CBO is limited. In earlier work, CBO was prepared as (dark) green colored powders, making it difficult to realize an optically transparent film suitable for dye sensitization.\textsuperscript{42, 43} Furthermore, the powders have a relatively high amount of impurities and are based on large particles, which is not suitable for application in a dye-sensitized photocathode. In addition, to the best of our knowledge there is no experimental evidence yet, neither from ultrafast spectroscopy nor photoelectrochemical studies, that CBO can indeed replace NiO.

In this work, we present a new procedure using a spin-coating technique modified relative to earlier methods,\textsuperscript{42} enabling to make semi-transparent CBO films showing a high surface area with a nanoparticle size around 10-20 nm. We found that the CuO impurities in the CBO films can be moderated by adjusting the precursor, the annealing temperature and annealing time. Ultrafast spectroscopy studies show that charge recombination in the CBO-based photocathode is significantly slower than in the NiO-based analogue. Photoelectrochemical experiments show a resulting 5-fold increase in photon-to-current efficiency, demonstrating the potential of CBO to replace NiO in dye-sensitized photocathodes.

7.2 Experimental

7.2.1 Preparation of photosensitized CBO films

The CBO films were prepared by a spin-coating method. To this end, 0.004 mol Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O (Sigma-Aldrich, Puriss. p.a. 99-104\%) was dissolved into 5 mL H\textsubscript{2}O, and 0.002 mol B\textsubscript{2}O\textsubscript{3} (Sigma-Aldrich, 99.98\%) was added into a mixed solution of 5 mL H\textsubscript{2}O and 4 mL 4 M HNO\textsubscript{3}. Different amounts of citric acid (CA, Sigma-Aldrich, >99.5\%, 0.004 mol, 0.008 mol and 0.012 mol) were added as a chelating agent to the mixed solution. Finally, 1 g of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (F108, Sigma-Aldrich) was added to the solution to increase the viscosity for spin-coating. This precursor solution was spin-coated onto a cleaned Fluorine-doped Tin Oxide (FTO, Sigma-Aldrich) substrate using two steps: a speed of 0 rpm for 30 s. and a speed of 2000 rpm for 20 s., followed by high temperature (450°C, 500 °C and 550 °C) annealing in air for 1 h. Drop-coating was used to have a film thick enough for XRD measurements.

The as-prepared CBO films were soaked in 0.3 mM 4-(bis-4-5-(2,2-dicyano-vinyl)-thiophene-2-yl-phenyl-amino)-benzoic acid (P1, Dyenamo, Sweden) dye solution in ethanol (Supelco, >99.9 \%) overnight (~16 h) and finally washed by ethanol (BOOM, ethanol 100\%, tech.).
7.2.2 Characterization

X-ray diffraction (XRD, Bruker D2, Cu Kα source) was used to determine the crystal structures. Oxidation states were characterized by X-ray Photoelectron Spectroscopy (XPS, PHI Quantes). The film morphology and layer thickness were investigated by high-resolution scanning electron microscope (Zeiss MERLIN HR-SEM). A ThermoSci EVO600 spectrometer was used to collect the UV-vis data, the reflectance spectrum was recorded using an PerkinElmer Lambda 950S spectrometer using an integrating sphere. The light absorption efficiency (F_A) of P1 on CBO was calculated from F_A = (1-10^-A) × 100%, with A the absorbance in optical density (OD) of FTO/CBO/P1 corrected for the signal of FTO/CBO.

The setups used for the time-resolved photoluminescence (TRPL) and femtosecond transient absorption (TA) experiments were described in detail in previous work. In brief, a 532 nm Fianium laser with a pulse duration of ca. 300 fs was used as the excitation source for TRPL experiments and the emission was detected using a streak camera system (Hamamatsu, C10910). The TA experiments were performed using a 500 nm pump beam, generated from the 800 nm input from a Ti:Sa amplifier (Coherent, Legend Elite, 5 kHz repetition rate, pulse duration of 35 ± 1 fs FWHM) using an optical parametric amplifier (Coherent, Opera). A small fraction of the Ti:Sa amplifier output was sent through a mechanical delay stage, focused into a CaF_2 crystal (Newlight Photonics, 3 mm thickness) mounted on a continuously moving stage to avoid crystal damage, and finally through a 700 nm short-pass filter to generate the broadband probe. The relative polarizations of the pump and probe beams were set at 54.7° magic angle. TA data analysis was performed using the program Glotaran.

A VersaSTAT 3 potentiostat was used to evaluate the photoelectrochemical characteristics of a three-electrode cell under backside irradiation (i.e. through the glass/TCO) using a solar simulator equipped with an AM 1.5G filter (Newport, 1 sun intensity) and a filter blocking the UV component (<400 nm). An Au wire was used as the counter electrode, while an Ag/AgCl electrode was used as the reference electrode. Prior to the measurements, the phosphate buffer solution (PBS, pH = 7) was degassed by N_2 for more than 20 min. The data were performed using a scan rate of 5 mV/s, and scans were recorded from high to low potential.
7.3 Results and discussion

![Figure 1](image)

**Figure 1.** XRD patterns of CBO layers (a); Cu 2p XPS spectra of the CBO film at different depths (b).

An important challenge in the preparation of CBO is the existence of impurities. Figure 1a shows the XRD pattern of a drop-coated CBO film on glass. The sample shows three diffraction lines, at 36.4°, 42.3° and a weak one at 61.4°, which can be assigned to CuBO$_2$ according to JCPDS card number PDF#28-1256. With lowering the CA amount in the precursor solution and increasing the annealing temperature from 500 °C to 550 °C, two additional diffraction lines around 35.5° and 38.7° appear (Fig. S1), earlier also assigned to CuBO$_2$. However, as is clear from Figure S1, these two diffraction lines do not match with the JCPDS data for CuBO$_2$, instead CuO is known to have diffraction lines at 35.5° and 38.7° (JCPDS card number PDF#48-1548), which agrees with previously reported CuO impurities in CBO. Furthermore, the color of the films becomes darker along with the CuO impurities (Figure S1). As CuO is a black narrow bandgap semiconductor material, it is reasonable to assume that the higher annealing temperature and lower CA amount in the precursor solution cause phase segregation and lead to the formation of CuO impurities. XPS was used to investigate the oxidation states of the CBO film, the Cu 2p spectrum is shown in Figure 1b. It is obvious that the surface and sub-surface (around 20 nm depth, obtained by sputtering the surface with an Ar$^+$ beam) of the film have different Cu oxidation states. On the surface, the strong satellite peaks around 942 eV and 962 eV indicate the existence of Cu$^{2+}$. The peaks around 933.5 eV and 953.5 eV can be assigned to a mixture of Cu$^{2+}$ and Cu$^{+}$. The satellite peaks vanish by Ar$^+$ sputtering, and the XPS peaks shift from 933.5 eV and 953.5 eV, to 932.7 eV and 952.7 eV. The latter indicates the presence of mainly Cu$^+$ in the sub-surface, in agreement with the oxidation state of Cu in CuBO$_2$. The difference between the Cu surface and sub-surface oxidation states is likely due to surface segregation during annealing, which has been reported to occur in other inorganic thin film materials. Also dangling bonds and defects may play a role.
CuBOx: a potential alternative for NiO as a hole acceptor layer

Figure 2. Surface (a) and cross-sectional (b) scanning electron micrographs of the CBO film on FTO.

In addition to the existence of impurities, large particle sizes (μm size, see Figure S2) leading to a small surface area is a second important limitation for application of CuMO2 materials in dye-sensitized electrodes.42,54 Adding F108 to the precursor solution and post-annealing to burn off the polymer results in a network structure with small nanoparticle sizes (around 10-20 nm, Figure 2a), which is ideal for dye sensitization. However, due to the strong acidity of the precursor solution, multiple spin-coating steps cannot easily increase the thickness of the film. The one spin-coating step CBO layer is very thin (around 45 nm, Fig 2b). Though this thickness is less attractive for application in a dye-sensitized photocathodes due to the limited quantity of dye which can be loaded onto the surface, the CBO layer can be used to characterize the photophysical properties as a hole accepting material. The UV-vis spectra of the CBO films on FTO before and after photosensitization with a P1 dye are shown in Figure S3. It is possible to adsorb P1 on the CBO surface (Figure S3), albeit with a low absorbance due to the thin CBO film. The maximum light absorption efficiency $F_A$ of P1 on the CBO film, corrected for the CBO background signal, is around 10% as shown in Figure 3a.

Figure 3. Light absorption efficiency of P1 on the CBO film, corrected for the CBO background signal (a); Normalized photoluminescence decay at 670 nm of P1 dye on quartz and on CBO, recorded using 532 nm excitation (b).
Although CBO has a lower valence band position than NiO, a dye-sensitized solar cell based on a functionalized CBO photocathode was reported to show a more than 10 times lower short-circuit current than the NiO-based analogue. Whether efficient light-induced hole injection from a dye into the CBO is possible remains hence a key question. Time-resolved photoluminescence spectroscopy is a powerful tool to probe this process, as the occurrence of light-induced charge transfer quenches the photoluminescence of the dye. Figure 3b shows the time-resolved photoluminescence decay of P1 on quartz and on CBO after excitation of predominantly the P1 dye at 532 nm. In contrast to P1 on quartz showing an exponential photoluminescence decay, a Gaussian peak is observed for P1 on CBO, indicating efficient interfacial light-induced charge transfer occurring within the instrumental response time of the streak camera setup.

**Figure 4.** Transient absorption spectra at various time delays of CBO/P1 in air after excitation at 500 nm (a); kinetic traces at 527 nm and 560 nm (b) and comparison of kinetic traces of CBO/P1 and NiO/P1 in air at 610 nm (c). The solid lines present fits from target analysis.

To gain more insight in the photodynamics of the CBO/P1 photocathode, femtosecond transient absorption (TA) studies were performed. Figure 4a shows the TA spectra of CBO/P1 in air at various time delays after excitation at 500 nm, showing transient signals at similar wavelengths as NiO/P1 in air. The photoinduced ground state bleach of the P1 dye gives a broad negative signal <600 nm mirroring the absorption spectrum (Figure 4a). The P1 excited state (P1*) is known to give a positive absorbance band around 560 nm. Due to hole injection from P1* into the CBO, the intensity of the P1* absorption will decrease alongside with an increase in the characteristic absorption of P1* around 610 nm, resulting in a red-shift in TA spectrum. Hole injection for NiO-based systems in air typically occurs biphasic, either ultrafast within the instrumental response time (IRT, 100-150 fs) or in a time window of 1-20 ps. The gap between the TA kinetic traces at 527 nm and 560 nm (Figure 4b) is an indication for the ratio between the ultrafast and slow component, the large gap indicates that for CBO/P1 in air hole injection is slow and mainly occurs in an early ps time window.

Figure 4c compares the normalized kinetic traces of CBO/P1 and NiO/P1 at 610 nm, which signal is mainly due to P1* and indicative for the charge recombination dynamics. The CBO/P1 photocathode
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shows a slower decay, indicating slower charge recombination. A possible reason for the slower charge recombination is the higher hole conductivity of CBO, which reduces hole accumulation at the surface promoting recombination with P1*. To quantify the difference in photodynamics between CBO/P1 and NiO/P1 and account for the spectral overlap in TA signals, target analysis has been performed using the open source program Glotaran. The TA data are well described by the photophysical model shown in Figure S5, which assumes that all photoinduced hole injection occurs in an early ps time window (τ1 ~ 1 ps) and charge recombination occurs either with holes trapped at the CBO surface (τ2) and in parallel also with relatively mobile holes which are able to reach the CBO bulk (τ3). The obtained species associated spectra and lifetimes are presented in Figure S6 and Table S1. Although this model is likely a simplification of the reality, it describes the TA data well. Overall, these results show that CBO is a promising potential p-type semiconductor for dye-sensitized photocathodes.

Considering that we recently observed that water has a huge impact on the NiO surface and the photoinduced charge transfer processes with P1, TA studies of CBO/P1 in 0.1 M phosphate buffer solution (PBS, pH = 7) were also performed (Figure S7). The much smaller gap between the transient signals at 527 nm and 560 nm as compared to Figure 4b indicates that aqueous conditions accelerate photoinduced hole injection from the P1 dye into the CBO, the same as in NiO/P1, i.e. in this case most hole injection occurs within the instrumental response time (100-150 fs), but the charge recombination is still lower than NiO/P1 in air (Figure S7b). This effect is likely due to the formation of surface OH· on the CBO, promoting hole injection as we also observed for NiO/P1.

![Figure 5](image_url)

**Figure 5.** Photoelectrochemical performance with 1 sun backside illumination (AM 1.5G, >400 nm) of CBO and CBO/P1 in 0.1 M PBS at pH = 7. Linear sweep voltammogram with chopped illumination at 10 mV/s (a) and i-t curves at -0.35 V vs. Ag/AgCl (b).

To further evaluate the performance of the P1-sensitized CBO photocathode, the photocurrent was
measured in 0.1 M phosphate buffer solution (PBS, pH = 7) with an Ag/AgCl reference electrode and an Au counter electrode. The results are shown in Figures 5 and S8. Figure 5a shows the current with chopped illumination while decreasing the applied potential from +0.1 V to -0.7 V vs. Ag/AgCl. Clearly a minimum can be observed in the j-V curve around -0.15 V, which we assign to (partial) reduction of copper oxide. The bare CBO film does not show a significant photo-response after stabilizing. When the P1 dye is attached to the CBO, a photocurrent is observed. The photo-response is best analyzed at potentials more negative than -0.2 V, and includes a capacitive current at -0.25 V.\textsuperscript{57} Not considering this capacitive current, the photo-response is approximately 15 μA/cm\textsuperscript{2} at -0.25 V, while decreasing to 10 μA/cm\textsuperscript{2} at -0.35 V. This decrease is hard to explain and is likely associated with voltage dependent surface compositional changes, such as the degree of hydroxylation. The photocurrent of CBO/P1 is more clearly apparent in chronoamperometry, at 10 μA/cm\textsuperscript{2} at -0.35 V vs. Ag/AgCl (see Figure 5b), with only maximal 10\% light absorption efficiency (Figure 3a).

To demonstrate the promise of the CBO-based electrode, the photocurrent of P1-sensitized NiO measured under the same conditions is included in Figure 5b. Even though the NiO is thick enough (~2 μm) enabling a high dye loading with ~90\% light absorption efficiency at the P1 absorption maximum (Figure S9), the photocurrent density is similar as for CBO/P1, despite the much lower dye loading of the latter. The photocurrent density is an indication of the photocathode performance and depends on the product of light absorption, charge separation efficiency and electron injection efficiency (from the dye into the electrolyte).\textsuperscript{39} As the electrode/electrolyte interface is the same as for NiO/P1, i.e. both P1/PBS, the photocurrent is in this case proportional to the product of the light absorption efficiency and charge separation efficiency. The approximately comparable photocurrent densities for NiO/P1 and CBO/P1, hence indicate an about 9 times higher photon-to-current efficiency for the latter.
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Figure 6. Surface (a) and cross-sectional (b) scanning electron micrographs of a FTO/NiO/CBO film; UV–vis absorbance spectra of a NiO/CBO layer without and with P1 dye (c); Light absorption efficiency of P1 on the NiO/CBO film corrected for the NiO/CBO background signal (d); Photoelectrochemical performance with 1 sun backside illumination (AM 1.5G, >400 nm) of NiO/CBO/P1 and NiO/P1 in 0.1 M PBS (pH=7) at -0.35 V vs. Ag/AgCl (e).

Despite the attractive 9-fold increase in photon-to-current efficiency of CBO/P1 photocathodes, there are also some remaining challenges. The thickness of the CBO films limits the dye loading and therefore hinders the performance of the dye-sensitized photocathode. However, it can be potentially used as a hole transport layer instead of NiO in perovskite solar cells, as inorganic photoelectrode or as an additional layer on top of NiO in a dye-sensitized photocathode. Figures 6a and 6b show surface and cross-sectional scanning electron micrographs of a NiO/CBO film on an FTO substrate, demonstrating that the CBO coating does not significantly change the structure of the NiO underlayer (scanning electron micrographs of NiO on FTO are shown in Figure S10), although it seems to slightly reduce the porosity. EDX mapping indicates that the CBO is uniformly coated on the NiO (Figures
S10 and S11). The thickness of this NiO/CBO film allows sufficient dye loading, resulting in a light absorption efficiency higher than 90% (Figures 6c and 6d), comparable to that of NiO/P1 (Figure S9). The photocurrent density of NiO/CBO/P1 is about two-fold higher than that of NiO/P1 (Figure 6e), indicating the CBO coating reduces surface charge recombination, in agreement with Figure 4c. The photocurrent drop during the initial 5 min. is likely caused by the instability of the CBO, which turns black during the measurement (Figure S12). This color change is likely due to reduction of surface CuO impurities, observed around -0.15 V vs. Ag/AgCl (Fig. 6a), and resulting phase segregation. This problem could be solved by preparing a pure CBO film without any Cu$^{2+}$ present especially at the surface (Figure 1b), or attempting to move the electron away from the CBO surface prior to Cu$^{2+}$ reduction by coating an additional electron transfer layer like TiO$_2$ or CdS (demonstrated in Figure S12). We should admit that this CBO material is not yet flawless, but present work demonstrates it has the potential to replace NiO as a superior hole transport layer.

7.4 Conclusions

In summary, we have prepared semi-transparent nanoporous CBO films on FTO substrates by using a sol-gel spin-coating method. The CBO film has a large surface area, suitable for application in a dye-sensitized photocathode. Photophysical analysis of a dye-sensitized CBO photocathode by time-resolved photoluminescence and femtosecond transient absorption spectroscopy demonstrate that the prepared CBO material has great potential to replace NiO, presently widely used as a p-type hole accepting metal oxide semiconductor. Photoelectrochemical studies show that the photon-to-current efficiency is 9-fold compared to that for NiO/P1 analogues, illustrating the promise of CBO in dye-sensitized photocathodes and presumably also in other applications.
Supporting Information

**Figure S1.** XRD patterns of CBO films prepared with different amounts of citric acid (CA) added to the precursor solution and various annealing temperatures for 1 hour, insert are the photographs of the CBO films prepared at these different conditions.

Figure S1 shows the XRD patterns of CBO films prepared with different amounts of citric acid (CA) added to the precursor solution and various annealing temperatures for 1 hour, demonstrating that the amount of CuO impurities depends on the annealing conditions. Figure S2 shows SEM images from literature of CBO layers, demonstrating large particle sizes limiting the surface area of these layers.
Figure S2. SEM images of CBO from ref. 38, 42 and 62.
Figure S3. UV–vis absorbance spectra of a CBO layer on FTO/glass without and with P1 dye.

Figure S4. Reflectance spectrum of the FTO/glass substrate.

Figure S3 shows the UV-vis absorbance spectra of a CBO layer without and with P1 dye adsorbed on the surface. The spectra of bare CBO on FTO show an increase in the near-infrared, likely due to the reflectance of the FTO substrates (Figure S4). The trends in Figure S4 are possibly shifted compared to those in Figure S3 due to the different n (λ) of CBO and air, and/or small variations in CBO layer thickness.
Figure S5. Photophysical model used for target analysis of the transient absorption data of CBO/P1 in air; IRT = instrumental response time.\textsuperscript{21}

Figure S5 shows the photophysical model used for target analysis of the transient absorption data of CBO/P1 in air.\textsuperscript{21} It assumes that all photoinduced hole injection from P1\textsuperscript{*} into CBO occurs in an early ps time window (\(\tau_1\)) and charge recombination occurs either between P1\textsuperscript{*} and h\textsuperscript{+} at the CBO surface (\(\tau_2\)) and in parallel also with h\textsuperscript{+} that have already reached the CBO bulk (\(\tau_3\)).\textsuperscript{21} Although this model is likely a simplification of the reality, it describes the TA data well. Table S1 presents the obtained lifetimes, the corresponding species associated spectra are presented in Figure S6. The red-shift in time is due to hole injection from P1\textsuperscript{*} into CBO, while the signals subsequently decay due to charge recombination (see main text).

Figure S6. Species associated spectra (SAS) obtained from target analysis of the transient absorption data of CBO/P1 in air. Note that \(\tau_3\) is longer than the experimental time window and therefore not accurate.
Table S1. Lifetimes of CBO/P1 in air from target analysis and compared with NiO/P1 in acetonitrile and air.\textsuperscript{21}

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\tau_1) (fs)</th>
<th>(\tau_2) (ps)</th>
<th>(\tau_3) (ps)</th>
<th>(\tau_4) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBO/P1 in air</td>
<td>938±13</td>
<td>9.8±0.1</td>
<td>742±9.8</td>
<td>-</td>
</tr>
<tr>
<td>NiO/P1 in acetonitrile</td>
<td>1270±28</td>
<td>11±0.2</td>
<td>370.8±11.4</td>
<td>-</td>
</tr>
<tr>
<td>NiO/P1 in air</td>
<td>690±12</td>
<td>5.7±0.1</td>
<td>56.1±1.4</td>
<td>(\infty)</td>
</tr>
</tbody>
</table>

Figure S7. Transient absorption kinetic traces at 527 nm and 560 nm of CBO/P1 in phosphate buffer solution (PBS, pH = 7) after photoexcitation at 500 nm (a) and Comparison of kinetic traces of CBO/P1 in air and PBS and NiO/P1 in air at 610 nm (b). The solid lines present fits from target analysis, using the photophysical model for aqueous conditions used earlier for NiO/P1.\textsuperscript{21}
**Figure S8.** Photoelectrochemical performance with 1 sun (AM 1.5G, >400 nm) of CBO in 0.1 M phosphate buffer solution (PBS) at pH = 7.

Figure S7 presents the transient absorption kinetic traces at 527 nm and 560 nm of CBO/P1 in phosphate buffer solution (PBS, pH = 7). As compared to CBO/P1 in air (Figure 5b main text), the gap between these signals has decreased substantially. This indicates that rather than in ~1 ps (Table S1, $\tau_1$) light-induced hole injection from P1 into CBO is accelerated when the photocathode is immersed into PBS, as also observed earlier for NiO-based systems and assigned to surface OH$^-$ species.\(^{21}\) Figure S8 shows the photocurrent of bare CBO in PBS at various applied potentials under chopped illumination. In the first scan, it shows a light response and photocurrent, which gradually disappears after a few scans. This photocurrent is likely from CuO impurities; CuO is a well-known unstable photocathode.\(^{61}\)
**Figure S9.** Surface (a) and cross-sectional (b) scanning electron micrographs of the NiO film on FTO; UV–vis absorbance spectra of a NiO layer without and with P1 dye (c); Light absorption efficiency of P1 on the NiO film, corrected for the NiO background signal (d).

**Figure S10.** Scanning electron micrographs and EDX results of NiO (a,c) and NiO/CBO (b,d).
Figure S11. EDX mapping of NiO/CBO.

Figure S12. Photoelectrochemical performance with 1 sun (AM 1.5G, >400 nm) of CBO/P1 and CBO/P1/CdS in 0.1 M phosphate buffer solution (PBS) at pH = 7.

Figure S9 presents surface and cross-sectional scanning electron micrographs of the NiO film on FTO, the UV–vis absorbance spectra of a NiO layer without and with P1 dye and the light absorption efficiency of P1 on the NiO film corrected for the NiO background signal. Figure S10 presents scanning electron micrographs and energy dispersive x-ray (EDX) results elemental mapping of the NiO and NiO/CBO films, the EDX mapping is shown in Figure S11. Figure S12 presents the
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photoelectrochemical performance of CBO/P1 and CBO/P1/CdS, both in PBS. The latter photocathode does not turn black in time alike the CBO/P1 photocathode (inset photographs), likely as a result of CdSe suppressing light-induced Cu\(^{2+}\) reduction occurring especially at the CBO surface, as also the negative signal around -0.15 V vs. Ag/AgCl has disappeared.

References


23. Massin, J.; Bräutigam, M.; Bold, S.; Wächtler, M.; Pavone, M.; Muñoz-García, A. B.; Dietzek,
CuBox: a potential alternative for NiO as a hole acceptor layer


CuBOX: a potential alternative for NiO as a hole acceptor layer

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CHAPTER 8

Summary and Perspective
Summary

In this PhD research, the dye-sensitized photocathode for solar fuel applications has been studied. P-type NiO is the most widely used semiconductor in the dye-sensitized photocathode. However, poor hole properties such as a low mobility and surface hydroxylation of NiO lead to fast interfacial charge recombination with the light-absorbing dye after photoinduced charge separation, resulting in a low photon-to-current efficiency. Therefore, it is important to develop fundamental understanding of the functionalized NiO and optimize it to improve the photocathode efficiency. Also the development of new p-type materials with suitable band gap, valence band position and a higher hole mobility than NiO is attractive.

In this PhD research, the performance of several dye-sensitized photocathodes in the formation of hydrogen by reduction of H⁺ has been evaluated and correlated to photophysical properties. In particular the unfavorable properties of p-type NiO have been addressed, to resolve poor hole mobility and optimize surface hydroxylation of NiO to prevent fast interfacial charge recombination after light-absorption by the surface immobilized dye, resulting in a low photon-to-current efficiency.

Ion substitution is a common strategy to tune material properties and Cu doped NiO shows promising results as a hole transport layer in perovskite solar cells and inorganic photoelectrodes. In Chapter 3, the effects of Cu doping of NiO sensitized with the well-known P1 dye are described. Photocathodes prepared from 9 mol% Cu in the precursor solution show the highest photocurrent density improvement relative to the undoped analogue. Femtosecond transient absorption spectroscopy studies show that the P1 sensitized Cu:NiO shows slower charge recombination than P1 sensitized NiO. The superior performance of the Cu-based photocathode is likely due to less dominant detrimental surface charge trapping and recombination, increasing the probability for holes to escape into the Cu:NiO bulk essential to reach the charge collection electrode and provide for a photocurrent.

Chapter 4 focuses on the charge transfer and recombination dynamics of the same NiO/P1 cathode in three different environments: air, PBS and acetonitrile. Not only light-induced hole injection but also interfacial charge recombination is slower when NiO/P1 is exposed to dry acetonitrile with a low amount of water. In air with high humidity or a water based environment, both light-induced hole transfer and the charge recombination rate are promoted. This is likely due to surface hydroxylation of NiO and formation of Ni(OH)₂, a good hole storage material with adaptive energy levels. As a result, the OH⁻ quantity on the NiO surface influences the hole injection rate and hole accumulation. Since NiO has a low hole mobility, this surface accumulation also promotes charge recombination. Therefore, it is important to balance the surface OH⁻ quantity of a dye-sensitized NiO photocathode in different working environments.
In photoelectrochemical solar fuel applications, an external bias is usually applied. Some studies have shown that a negative potential can promote hole injection as well as reduce charge recombination of dye-sensitized NiO in acetonitrile. However, it is unclear whether similar or different behavior applies to an aqueous electrolyte. Chapter 5 focuses on the effect of the external bias on the photodynamics of NiO/P1 in PBS by in-situ time-resolved photoluminescence and femtosecond transient absorption spectroscopy. Under more negative potential, slower charge recombination is indeed observed. However, the hole injection rate is also decreased, instead of accelerated as reported in earlier studies. The synchronous decrease or increase of the hole injection and charge recombination rate is in line with the dual role of surface OH discussed in chapter 4. The external potential applied to the electrode changes the electrochemical double layer. Therefore, the negatively charged NiO based electrode attracts H\(^+\) and the positive charged electrode attracts OH\(^-\) into the inner Helmholtz plane, explaining the trends in the photodynamics observed with applied bias. This result also suggests that tuning the ions in the electrolyte may enable to tune the photoelectrochemical performance.

In the research described in Chapter 6, myristic acid (MA) with a carboxyl anchoring group and a long apolar alkyl chain was co-adsorbed with the P1 dye on the NiO surface. Transient absorption shows that with co-adsorption of MA, both hole injection and charge recombination are slowed down, likely due to the hydrophobic nature of MA. Interestingly, we observed that the presence of MA inhibits the P1 twisting after photoexcitation, which enhances the electrochemical potential of electrons from reduced P1 dye molecules and enables H\(_2\) evolution without additional proton reduction catalyst. We assign this observation to a synergistic effect of inhibited twisting of the P1 dye increasing the electrochemical potential of electrons available for the reduction reaction. While the experimental data do provide evidence for a specific active site, the formation of H\(_2\) upon illumination appears associated with a high quantity of adsorbed H\(^+\) on the NiO surface.

Chapter 7 focuses on the p-type semiconductor CuBO\(_2\), which may be an attractive alternative to NiO. The photophysical and photoelectrochemical properties of CuBO\(_2\) have hardly been studied experimentally, even though CuBO\(_2\) has been reported to have a 10 times higher hole mobility than other CuMO\(_2\) analogues (M=Al, Cr, Ga) and NiO, and a deeper valence band position. The difficult synthesis to achieve a CuBO\(_2\) film with good optical transparency and large surface area and the lack of fundamental understanding of its properties are likely the reasons for this lack of attention. By modifying earlier reported preparation methods, we successfully prepared semi-transparent CuBO\(_2\) films with a nanoparticle size around 10-20 nm. Ultrafast spectroscopy studies show that charge recombination in the CuBO\(_2\)-based photocathode is significantly slower than in the NiO-based analogue. Photoelectrochemical experiments show a resulting 9-fold increase in photon-to-current efficiency, demonstrating the potential of CuBO\(_2\) to replace NiO in dye-sensitized photocathodes and other applications. Some remaining challenges, such as a phase changes during operation and a thin film thickness, are also discussed.
**Perspective**

Dye-sensitized photoelectrochemical cells show great potential in solar fuel generation, but there are still many opportunities for improvement. Future research should focus on fundamental understanding of the charge carrier dynamics at the semiconductor/dye-catalyst/electrolyte interface to optimize the design of the electrode structure and photoelectrochemical devices. At the end of this thesis, I propose research directions I consider as important and worth to spend time on.

**NiO facets**

![NiO Facets Diagram](image)

**Figure 8.1.** Crystal morphologies exposing a range of \{hkk\} facets.\(^1\)

The rapid charge recombination is the primary problem of NiO-based photocathodes. As discussed in chapters 3 and 4, surface hydroxylation and the low hole mobility of NiO play a significant role here. Different NiO facets have various atomic arrangements, which affects the surface hydroxylation and hole conductivity.\(^2\)-\(^3\) For example, the NiO (111) facet is more conductive and sensitive to H\(_2\)O adsorption than the NiO (100) facet. However, which NiO facet, (111) or (100), performs better in a dye-sensitized photoelectrochemical cell is still debated.\(^2\)-\(^3\) Additionally, the NiO crystal with multiple exposed facets (see Figure 8.1) may develop an internal electric field, which might accelerate charge separation and improve the photoelectrochemical performance. Therefore, it is important to study the facet-dependent charge transfer dynamics of dye-sensitized NiO and the photoelectrochemical cell performance, although this could be experimentally challenging.
New p-type semiconductors

Figure 8.2. Transient absorption kinetic traces at 645 nm of NiO/P1, TiO$_2$/P1 and ZrO$_2$/P1 after 500 nm excitation.

The development of new p-type semiconductors has been discussed in chapters 1 and 7. Here I like to highlight once more the importance. Figure 8.2 shows the transient absorption kinetic traces of P1-sensitized NiO, TiO$_2$ and ZrO$_2$ after 500 nm excitation. The signal either mainly represents P1$^-$ after hole injection into NiO (black), predominantly P1$^{+\cdot}$ after electron injection into TiO$_2$ (red) or mostly P1$^*$ after photoexcitation (on ZrO$_2$, blue). Obviously, the decay is the fastest for NiO/P1 and the slowest for TiO$_2$/P1, indicating significantly faster interfacial charge recombination in NiO/P1 than in TiO$_2$/P1. This also explains why dye-sensitized photoanodes outperform photocathodes. The p-type semiconductor rather than the dye or catalyst is the main cause for the fast charge recombination and poor performance. Even though we demonstrated in chapter 7 that CuBO$_2$ prolongs the charge separation lifetime compared to NiO, there is still a lot of space for improvement as compared to TiO$_2$.

Nano-array conductive substrates

In the dye-sensitized photoelectrode, a relatively thick inorganic semiconductor layer based on for example NiO or TiO$_2$ is required to achieve a high dye loading and sufficient light absorption. However, the thick film also requires a long charge diffusion length, and promotes charge recombination especially for NiO. One of the strategies to reduce the required charge diffusion length but not decrease the dye loading is to use nano-array conductive substrates. Due to the larger surface area of the nano-array substrate compared to a planar substrate, a relatively thin semiconductor layer allows sufficient dye loading. Additionally, nanostructured electrodes can collect sunlight more efficiently due to light trapping effects.
The design of novel dyes

In chapter 6, we observed that co-adsorption of MA with a long apolar alkyl chain can prevent the photoinduced twisting of the P1 donor-acceptor dye and increase the electrochemical potential of the electron available for the reduction reaction. Very importantly, this enables to generate H₂ in the absence of an additional catalyst. Therefore, more studies on the relationship between the structural flexibility of molecules and the performance should be carried out. Strategies like alkyl cyclization can be used to reduce the structural flexibility of the dye and study the structure-activity relationship. As the co-adsorption of MA caused a reduction in light absorption efficiency, instead of MA. Perhaps an apolar chromophore can be developed, that differs from the primary dye in terms of its UV-vis absorption spectrum. In the ideal case, one should combine an apolar environment with optimal overlap with the solar emission spectrum.

References

Samenvatting

In dit promotieonderzoek is de kleurstofgesensibiliseerde fotokathode bestudeerd, die in detail wordt beschreven in Hoofdstuk 1. Deze fotokathode is onderdeel van een fotoelectrochemische cel, die onder belichting direct duurzame brandstof kan produceren zonder elektriciteit als tussenproduct, hetgeen zeer aantrekkelijk is i.v.m. opslag. Voor grootschalige toepassing is het echter wel van belang om de efficiëntie te verhogen, waarvoor fundamenteel begrip van lichtgeïnduceerde processen van belang is. P-type NiO is de meest gebruikte halfgeleider in deze fotokathodes, op het NiO oppervlak wordt een licht absorberende kleurstof aangebracht. Onder belichting injecteert de kleurstof een positieve lading (gat) in het NiO, zogenaamde foto-geïnduceerde ladingsscheiding, gevolgd door de overdracht van een elektron naar de katalysator die bijvoorbeeld CO2 in brandstof omzet. De lage mobilitieit van gaten en oppervlakte hydroxylering van NiO leiden echter tot snelle ladingsrecombinatie met de kleurstof na foto-geïnduceerde ladingsscheiding, hetgeen resulteert in een lage efficiëntie. Om efficiënte fotokathodes te realiseren, is fundamenteel begrip van het systeem essentieel. Mogelijk zijn er ook nieuwe materialen die NiO kunnen vervangen, zeker als ze een geschikte valentieband positie hebben en een hogere gatenmobilitie dan NiO. De gebruikte experimentele technieken worden besproken in Hoofdstuk 2.

Ionensubstitutie is een gebruikelijke strategie om materiaaleigenschappen aan te passen en Cu-gedoteerd NiO laat veelbelovende resultaten zien als gaten transportlaag in perovskiet zonnecellen en anorganische fotoelektrodes. In Hoofdstuk 3 worden de effecten van Cu-dotering van NiO gefunctionaliseerd met de bekende P1-kleurstof beschreven. Fotokathodes bereid uit 9 mol% Cu in de precursoroplossing vertonen de hoogste verbetering van de fotostroomdichtheid ten opzichte van de niet-gedoteerde fotokathode. Femtoseconde transient absorptie spectroscopie studies laten zien dat de met P1 gefunctionaliseerde Cu:NiO fotokathode een langzamere ladingsrecombinatie vertoont dan die op basis van NiO. De superieure prestaties van de Cu-gedoteerde fotokathode zijn waarschijnlijk te danken aan minder sterke ophoping van gaten op het grensvlak met de kleurstof, waardoor de kans op ladingsrecombinatie afneemt en de fotostroomdichtheid verbetert.

Hoewel de Cu-gedoteerde fotokathode in fosfaatbufferoplossing (PBS) langzamere ladingsrecombinatie en een hogere fotostroomdichtheid heeft dan de niet gedoteerde fotokathode, is de efficiëntie van een kleurstofgesensibiliseerde zonnecel in een elektrolyt op basis van acetonitril met 3I-/I3- redoxkoppel lager voor het Cu-gedoteerde systeem. Om dit te kunnen begrijpen, richt het onderzoek beschreven in Hoofdstuk 4 zich op de ladingsoverdracht en recombinatiedynamiek van hetzelfde NiO/P1 in drie verschillende omgevingen: PBS, lucht en droge acetonitril. Zowel de snelheid waarmee de belichte kleurstof gaten injecteert in het NiO als de ladingsrecombinatie blijken sterk van de omgeving af te hangen. Deze processen zijn beide het snelste in een waterige oplossing en
het traagste in droge acetonitril. Deze verschillen komen waarschijnlijk door oppervlakte hydroxylering van NiO naar Ni(OH)\textsubscript{2}, het laatste materiaal heeft andere energieniveaus dan NiO en kan goed gaten opslaan. Aangezien NiO een lage gaten mobiliteit heeft, bevordert deze oppervlakteaccumulatie echter ook ladingsrecombinatie. Daarom is het in verschillende werkomgevingen steeds van belang om de hoeveelheid OH\textsuperscript{-} op het oppervlak van het NiO te optimaliseren.

In fotoelectrochemische cellen wordt meestal gebruik gemaakt van een externe potentiaal. Sommige onderzoeken hebben aangetoond dat een negatieve potentiaal de lichtgeïnduceerde injectie van gaten van de kleurstof in het NiO kan bevorderen en ladingsrecombinatie kan verminderen, deze studies waren echter aan zonnecellen met een acetonitril gebaseerde elektrolyt met 3I\textsuperscript{-}/I\textsuperscript{3-} redoxkoppel. Het is onduidelijk of vergelijkbaar of ander gedrag van toepassing is in een waterige elektrolyt, relevant voor fotoelectrochemische cellen. Hoofdstuk 5 richt zich daarom op het effect van de externe potentiaal op de fotodynamica van NiO/P1 in PBS door in-situ tijdsopgeloste fotoluminescentie en femtoseconde transiente absorptie spectroscopie studies. Bij een meer negatieve potentiaal wordt inderdaad langzamere ladingsrecombinatie waargenomen. De snelheid waarmee de belichte kleurstof gaten injecteert in het NiO wordt echter ook lager, in plaats van hoger zoals beschreven in eerdere studies. Deze synchrone afname of toename van de snelheid waarmee lichtgeïnduceerde gatinjectie door de kleurstof in het NiO en ladingsrecombinatie plaatsvinden is in overeenstemming met de dubbele rol van oppervlakte OH\textsuperscript{-} zoals besproken in Hoofdstuk 4. De externe potentiaal die over de elektrode wordt aangelegd verandert de elektrochemische dubbellaag. Een negatief geladen elektrode trekt H\textsuperscript{+} aan in het binnenste Helmholtz-vlak, een positief geladen elektrode OH\textsuperscript{-}. Dit resultaat geeft aan dat de ionen in het elektrolyt een belangrijke rol spelen, en het veranderen daarvan het wellicht mogelijk maakt de fotoelectrochemische eigenschappen van de fotokathode verder te verbeteren.

Eerder in Hoofdstuk 4 werd beschreven hoe belangrijk het is om in verschillende werkomgevingen de hoeveelheid oppervlakte-OH\textsuperscript{-} steeds te optimaliseren. In een waterige elektrolyt is het verminderen van de hoeveelheid oppervlakte geadsorbeerde water belangrijk om de hoeveelheid OH\textsuperscript{-} te reguleren en snelle ladingsrecombinatie te verminderen. In het onderzoek beschreven in Hoofdstuk 6 werd myristinezuur (MA) met een carboxyl verankerende groep en een lange apolaire alkyl keten samen met de P1-kleurstof geadsorbeerde op het NiO-oppervlak. Femtoseconde transiente absorptie metingen laten zien dat door de co-adsorptie van MA zowel lichtgeïnduceerde gatinjectie van de kleurstof in het NiO als ladingsrecombinatie worden vertraagd, waarschijnlijk door de hydrofobe aard van het MA. Een heel interessante observatie is dat de aanwezigheid van MA leidt tot de vorming van waterstofbelletjes onder belichting, zelfs in de afwezigheid van een katalysator. We kennen dit toe aan een synergetisch effect van minder verdraaiing van de P1-kleurstof na lichtabsorptie, waardoor de elektrochemische potentiaal van elektronen die beschikbaar zijn voor de reductiereactie wordt verhoogd, gecombineerd met H\textsuperscript{+} geadsorbeerde op het NiO oppervlak.
Hoofdstuk 7 richt zich op de p-type halfgeleider CuBO₂, die een aantrekkelijk alternatief kan zijn voor NiO. De fotofysische en fotoelectrochemische eigenschappen van CuBO₂ zijn nauwelijks experimenteel bestudeerd, ook al is beschreven dat CuBO₂ mogelijk een 10 keer hogere gatenmobiliteit heeft dan andere CuMO₂-analogen (M=Al, Cr, Ga) en NiO, gecombineerd met een diepere valentiebandpositie. De lastige synthese om een nanogestructureerde CuBO₂ film met een goede optische transparantie en een groot oppervlak voor genoeg kleurstof adsorptie te verkrijgen en het gebrek aan fundamenteel begrip van de eigenschappen ervan zijn waarschijnlijk de redenen voor dit gebrek aan aandacht. Door eerder gepubliceerde bereidingsmethoden aan te passen, hebben we met succes semi-transparante CuBO₂ films gemaakt met een deeltjesgrootte van ongeveer 10-20 nanometer. Ultrasnelle spectroscopie metingen tonen aan dat ladingsrecombinatie in de CuBO₂-gebaseerde fotokathode aanzienlijk langzamer is dan in de NiO-gebaseerde fotokathode. Fotoelektrochemische experimenten tonen een 9-voudige toename in efficiëntie als resultaat, wat het potentieel aantoont van CuBO₂ om NiO te vervangen in kleurstofgesensibiliseerde fotokathodes en andere toepassingen. Enkele resterende uitdagingen, zoals een faseverandering tijdens gebruik en een dunne laag dikte, worden ook besproken.

In Hoofdstuk 8, tot slot, wordt het onderzoek samengevat en verschillende ideeën gepresenteerd voor vervolgonderzoek.
List of Publications:


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Kaijian Zhu

朱凯健