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

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ABSTRACT: 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 (~10 ps) occurring more than 1 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.

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 efficiencies 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 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 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−perylene-monomide-sensitized NiO followed by fast (tens of picoseconds to several microseconds) 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, ~17, and ~205 ps).¹⁷

In addition to the dye and catalyst design, the properties of NiO and, in particular, surface defects are likely to play an

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important role in the fast charge recombination often observed.\textsuperscript{18–20} Unlike the dye and catalyst, modification of NiO has however gained less attention so far,\textsuperscript{3,21} although Li\textsuperscript{+},\textsuperscript{22,23} Mg\textsuperscript{2+},\textsuperscript{24,25} and Co\textsuperscript{2+}\textsuperscript{26} doping have been investigated by a number of groups and were observed to reduce charge recombination between NiO and dye. The band gap of NiO of 3.4–4.0 eV is assigned to the O 2p → Ni 3d electronic transition.\textsuperscript{27–30} The intrinsic p-type character of NiO is generally accepted to originate from the presence of Ni vacancies where holes could localize.\textsuperscript{28} Holes are likely surrounded by self-induced lattice distortions (polarons), and this self-trapping is hampering hole transport.\textsuperscript{31} 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.\textsuperscript{32} 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.\textsuperscript{33} 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 biggest 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.

EXPERIMENTAL SECTION

Preparation of Photosensitized NiO and Cu:NiO Films. NiO and Cu:NiO films were prepared by spin-coating. The precursor solution for NiO was prepared by dissolving 0.3 M Ni(NO$_3$)$_2$·6H$_2$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 (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.

Sample Characterization. The crystal structures were determined by X-ray diffraction (XRD) (Bruker D2, Cu Ka 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.

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 and focused into a Ti:sapphire amplifier cavity using a 100x microscope objective. The laser pulse was split into two beams using a 100:1 beam splitter and focused into the Ti:sapphire amplifier cavity using a 100x microscope objective. The laser pulse was then amplified using a 100x microscope objective. The amplified laser pulse was then split into two beams using a 100:1 beam splitter and focused into the Ti:sapphire amplifier cavity using a 100x microscope objective. The amplified laser pulse was then split into two beams using a 100:1 beam splitter and focused into the Ti:sapphire amplifier cavity using a 100x microscope objective. The amplified laser pulse was then split into two beams using a 100:1 beam splitter and focused into the Ti:sapphire amplifier cavity using a 100x microscope objective.

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.
time resolution is ca. 100 μs. The diode spectrometer was coupled to a home-built 256 pixels diode array through the sample, probe pulses were sent into a 15 cm long probe 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 ×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 analyzed using the open-source program Glotaran.35

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 an 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 an electron sacrificial agent. All of 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.

RESULTS AND DISCUSSION

Figure 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 Figure S1). Energy-dispersive X-ray spectroscopy analysis (EDS, Figure S2) confirms that 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.36–39 Nevertheless, strong visible light absorption is achieved for these layers sensitized with P1 dye (see Figure 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.

Figure 2a shows the XRD patterns of NiO and 9 mol % Cu:NiO layers on glass (causing the broad diffraction line around 2θ = 20–30°); (b) UV–vis spectra of the layers with and without P1 dye.

Figure 2. (a) XRD patterns of NiO and 9 mol % Cu:NiO layers on glass (causing the broad diffraction line around 2θ = 20–30°); (b) UV–vis spectra of the layers with and without P1 dye.
also result in an increase in interplanar spacing and lattice parameter, in agreement with earlier work. X-ray photoelectron spectroscopy (XPS, Figure 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.

Figure 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 a function of wavelength are shown in Figures S6 and S7. 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, Figure S8) gives a small decrease in band gap 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 band gap, 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 × 10^4 M\(^{-1}\) cm\(^{-1}\) at 468 nm. Relative to P1 in solution, P1-sensitized (Cu):NiO films show a broadening and red shift in absorbance, likely due to structural inhomogeneity and electronic coupling between a dye and a semiconductor, with a maximum around 500 nm as observed earlier (see Figure 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 (Supporting Information, Figure S9).

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 (Figure 3a), with the strongest improvement observed for 9 mol % Cu-doping. The photocurrents significantly exceed those of the layers without P1 (Supporting Information, Figure S10), demonstrating that the photocurrent mainly originates from P1 photoexcitation. For the Cu-doped sample, the photocurrent (and dark current) maximizes at $\sim -150 \mu A$ at around 0.45 VRHE. This current is likely the consequence of the reduction of Cu$^{2+}$ to Cu$^{+}$ (see cyclic voltammograms in Figure S11) 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$^{+}$, 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 (Figure 3c). An unexpected trend in Figure 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 Cu-doped photocathodes and 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 min, but then stabilizes. For the Cu:NiO-based photocathode, the photocurrent especially during the initial 3 min 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 ($\sim 13 \mu A/cm^2$ for NiO/P1 and $\sim 24 \mu A/cm^2$ for 9 mol % Cu:NiO/P1 at 0.31 V vs RHE). The stability is significantly higher than reported in earlier work (Figure 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, Figure S12), which is presumably due to the P1 dye degradation or desorption in the initial 3 min. 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 photocurrent conversion efficiency mainly depends on three factors: (i) light absorption efficiency, (ii) electron injection efficiency (from a dye to an electrolyte), and (iii) charge separation efficiency between a dye and NiO.55,56 The light absorption efficiency is not the reason for the enhancement as mentioned above. To decouple electron injection efficiency and charge separation efficiency, photocurrents were measured under similar conditions as in Figure 3a, but now with K2S2O8 as electron scavenger (Figure 3c).57,58 In this situation, all electrons photoexcited to the P1 LUMO are assumed to be captured by the electron scavenger (leading to the formation of sulfate, SO42−) 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 SO42−. Since the difference in photocurrent induced by Cu-doping of NiO remains, it should mainly originate from a difference in charge separation efficiency between the photoexcited dye and 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 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.
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 $\tau_1$, $\tau_2$, and $\tau_3$ are provided in Figure S14. The values for $\tau_1$, $\tau_2$, and $\tau_3$ 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).

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 band gap (Supporting Information, Figure S8). 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 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 coexistence of Cu$^{2+}$ and Cu$^{+}$ ions, as follows from XPS (Supporting Information, Figure S8), 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$^{3+}$ 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, which may also occur here. Holes in intrinsic NiO likely localize at Ni sites. 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. 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. 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, Figure S1). Also, the decrease in crystallite size due to Cu-doping (Supporting Information, Figure S5, and Table 1) may contribute to this optimum.

As NiO is a well-known material used as a supercapacitor, it has the ability to store charges at the interface between NiO and the electrolyte. 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 s (Supporting Information, Figure S15), with NiO showing a slower decay indicative of good charge storage ability. 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 mobile 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 nondecaying component ($\tau_1$) to long-lived trapped holes, which could lead to the formation of Ni$^{3+}$ and Ni$^{4+}$ centers absorbing in the visible. 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 of reaching the TCO electrode, leading to significant enhancements in photocurrent observed here.

## CONCLUSIONS

In the present work, we report photocurrents up to $\sim28 \mu$A/cm$^2$ at 0.05 V vs RHE for functionalized NiO-based photocathodes without a 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.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c03553.

Figures S1–S15 and Table S1 with explanatory text: photoelectrochemical performance at various mol % Cu-doping; stability testing; EDX result; XPS data; XRD data and fits; UV–vis absorbance spectra; Tauc plot; cyclic voltammograms; kinetic traces 9 mol % Cu:NiO/P1 photocathode; species-associated spectra from target analysis of the transient absorption data; and open-circuit voltage decay of NiO and Cu:NiO layers (PDF)
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Notes
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