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Light-Driven Electron Transfer between a Photosensitizer and a Proton-Reducing Catalyst Co-adsorbed to NiO

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Ⓢ *Supporting Information*

ABSTRACT: While intermolecular hole-hopping along the surface of semiconductors is known, there are no previous examples of electron-hopping between molecules on a surface. Herein, we present the first evidence of electron transfer from the photoreduced sensitizer Coumarin-343 (C343) to complex **1**, both bound on the surface of NiO. In solution, **1** has been shown to be a mononuclear Fe-based proton-reducing catalyst. The reduction of **1** is reversible and occurs within 50 ns after excitation of C343. Interfacial recombination between the reduced $\mathbf{1}^{(-)}$ and NiO hole occurs on a 100 μs time scale by non-exponential kinetics. The observed process is the first essential step in the photosensitized generation of H_2 from a molecular catalyst in the absence of a sacrificial donor reagent.

Dye-sensitized solar cells (DSSCs) have been investigated and developed extensively for use in photovoltaic devices.[1,2] However, their potential for solar fuels production is a very recent and still little explored subject.[3−6] A critical challenge is matching the rate of light-driven charge separation and transport with the catalytic steps of fuel formation and water oxidation. Catalysts for water oxidation have been attached directly to a TiO_2-bound sensitizer[3] or deposited in a separate Nafion layer on top of the TiO_2/dye film.[4,5] The former approach is more synthetically demanding, while the latter gives rather poor electron transport between the separate layers. For the corresponding H_2-forming reaction on p-type materials, there is only one study that used a dye/NiO film and a cobaloxime catalyst,[7] but the cobaloxime was free in solution and may therefore also act as a redox shuttle to the counter electrode to create current instead of H_2. In this paper, we investigate a different approach where we co-sensitize a mesoporous NiO film with both dye and catalyst. This relies on the possibility that, after electron transfer from NiO to the excited dye, efficient surface electron-hopping occurs between dye molecules and the catalyst.

From the field of DSSCs, hole transfer between molecules along the interface of semiconductors is known.[8,9] This occurs as a "hole-hopping" mechanism from donor molecules to acceptor molecules, allowing for charges to migrate over significant distances at the surface of semiconductors. This hole-transfer mechanism is mediated solely by non-covalent interactions between adjacent molecules. In dye-sensitized water oxidation, photosensitizer-to-photosensitizer hole-hopping is the likely mechanism to drive the cumulative hole-transfer chemistry.[4,5,10] However, to the best of our knowledge there exist no examples in the literature of light-driven "electron-hopping" between molecules on the surface of any semiconductor. We report on the first evidence for "electron-hopping" from a photosensitizer to a complex **1** co-adsorbed to a thin film of NiO. In solution, complex **1** is a proton-reducing catalyst.[11] All components are based on abundant elements. The described process is a first step in the photosensitized generation of H_2 from a molecular catalyst in the absence of a sacrificial reagent.

Designing chemical systems to take advantage of intermolecular charge-hopping has many benefits: (i) many sensitizers may transfer charge to a single acceptor; (ii) modular design allows the screening of different catalysts without elaborate synthesis; (iii) decreased reliance on robust bonds between a photosensitizer and catalyst; and (iv) decoupling light absorption events by a photosensitizer and the resulting catalysis.

For the proton-reducing catalyst **2** in Figure 1, molecular turnover frequencies >10 000 s^{-1} are reported.[11] However, the visible photon flux from sunlight is <1000 s^{-1} nm^{-2}.[12] To match the catalytic efficiency using sunlight to photo-initiate the reaction would require absorbing all visible photons on an area >10 nm^2. This is impossible if the photosensitizer and catalyst are covalently linked as a single molecule. Allowing for electron-hopping from a photosensitizer to the catalyst dramatically increases the number of photosensitizers that can contribute to the chemistry of a single catalyst.

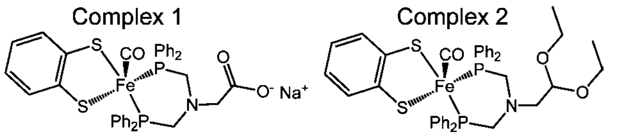

Figure 1. Complex **1** was functionalized with a carboxylate group for anchoring to NiO; the structurally analogous complex **2**[11] has a higher solubility in acetonitrile and is, in solution, a proton-reducing catalyst that operates at low overpotential.

The laser dye Coumarin-343 (C343) was used as the photosensitizer, since it has a high reduction potential in its one-electron-reduced state ($C343^{0/-}$; −2.1 V vs $Fc^{+/0}$) and is known to rapidly inject holes into NiO.[13−15] Complex **1** is

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identical to the previously reported complex **2** in the first and second coordination spheres around Fe,[11] but **1** contains a pendant carboxylate to bind to the surface of NiO (see Figure 1). Sequentially, C343 and **1** were bound to the surface of mesoporous NiO thin films. In transient absorption measurements for the co-adsorbed films, it was seen that, by exciting C343 with pulsed laser light, the radical anion of **1** was visible within 50 ns and recombined with NiO(+) on a time scale of 100 *μ*s.

NiO films were sensitized by immersion of films in Ar-saturated ethanolic solutions of C343 in the dark over a span of 2 days. After sensitization with C343, the NiO films were co-adsorbed with **1** by immersion in 3:1 methanol/acetonitrile solutions for 2 days in the dark and under an Ar atmosphere. As a control for sensitizing order, other films were sensitized first with **1** and second with C343. Through the co-adsorption process, a notable decrease in the UV−visible absorption of C343 on the surface of NiO films was observed as well as a small shift in the C343 absorbance to the red (Figure 2). A very basic calculation for the surface coverage of C343 on NiO, which is detailed in the Supporting Information, suggested 20% monolayer coverage. At 20% of a monolayer, the average C343−C343 distance is 6 Å. However, true C343−C343 distances may be much smaller due to clustering of C343 on the surface of NiO. We estimate the ratio of **1** to C343 on the surface of NiO to be between 1:2 and 1:4. Due to the small extinction coefficient of **1** in the visible, its absorption on the surface of NiO by UV−visible was weak (Figure 1 inset).

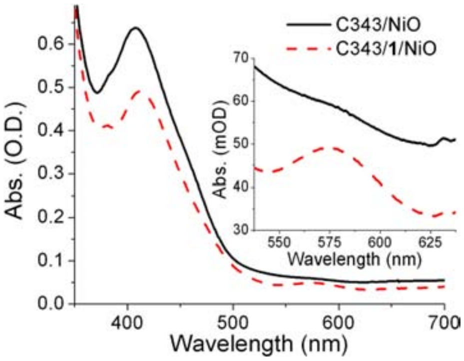

Figure 2. Absorption spectra of C343/NiO (solid) and C343/**1**/NiO (dashed). Inset: Magnification of the region of **1** absorption.

To verify that **1** binds to NiO, Raman measurements were made of C343-sensitized NiO films before and after slides were immersed in a solution of **1**. The IR spectrum of **1** in dichloromethane shows a $C\equiv O$ stretch at 1908 cm^{-1} (Figure S3). As seen in Figure 3, after immersion of NiO films in solutions of **1**, a new feature is observed at 1925 cm^{-1}.

We attribute the small differences in stretching frequencies between bound and unbound **1** to the differing environments. The $C\equiv O$ stretch is a characteristic vibration for **1**, and thus confirms its presence on the NiO films. The samples did not appear to be photolabile and showed no damage from prolonged laser excitation at 514 nm (see Figure S4). However, exposure of C343/**1** co-adsorbed films to air resulted in the loss of the Raman feature at 1925 cm^{-1} in <2 min, indicating oxidative degradation of **1** with concomitant CO loss.

Due to poor solubility of **1**, electrochemistry and spectroelectrochemistry were performed on the previously studied analogue **2**.[11] Both **1** and **2** have two peaks in their visible absorption spectra (430 and 580 nm), as seen in Figures 4 and S4. Single-electron reduction of **2** ($E^0 = -1.66$ V vs $Fc^{+/0}$) led to an increase in the absorbance at ∼500 nm and a decrease for the peaks of the neutral species.

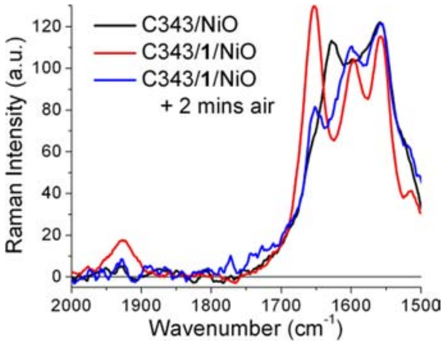

Figure 3. Raman spectra of NiO films adsorbed with C343 (black line) and C343/**1** (red line) acquired at 514 nm excitation. Binding **1** to NiO resulted in new vibrations at 1925 and 1650 cm^{-1}; exposure to air for 2 min (blue line) resulted in the loss of those vibrations.

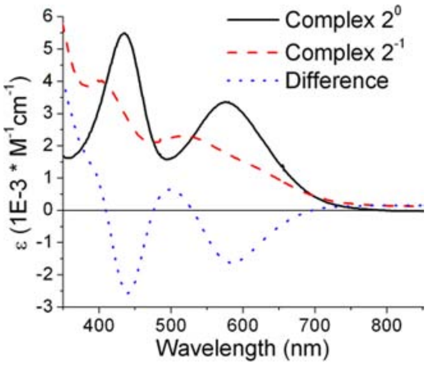

Figure 4. Reducing complex **2** by one electron (**2**(−), red dashed line) resulted in decreases in the absorbance of the neutral state (**2**, black solid line). The difference between the **2**(−) and **2** spectra (blue dotted line) represents the contributions of **1** to the transient spectra in Figure 5.

To confirm light-driven electron transfer from photoreduced C343(−) to **1** co-adsorbed to the surface of NiO, nanosecond transient absorption measurements were performed. For NiO thin films that were co-adsorbed with both C343 and **1**, the transient absorption spectra after excitation of C343 (460 nm, 9 mJ cm^{-2}, 8 ns fwhm) resulted in a bleach at 430 nm, a peak at 500 nm, and a broad absorbance throughout the near-IR within the time resolution of our instruments, 50 ns (Figure 5). When comparing these spectral features with the spectroelectrochemistry on **2** and literature values for NiO,[16,17] these transient absorbance signals are consistent with the formation of **1**(−) and NiO(+). The signals returned to baseline over the span of 100 *μ*s following nonexponential kinetics (Figure S5). The order in which C343 and **1** were bound to the surface of NiO did not affect observation of these signals (Figures 5 and S5). The transient spectra showed a high degree of reproducibility over the length of the experiment: about 1800 laser flashes (Figure S6). The absorbance of **1** is insignificant at the excitation wavelength (460 nm) and does not contribute to the observed signal.

As a control experiment, we measured transient absorption spectra from the excitation of C343 bound to NiO under an Ar

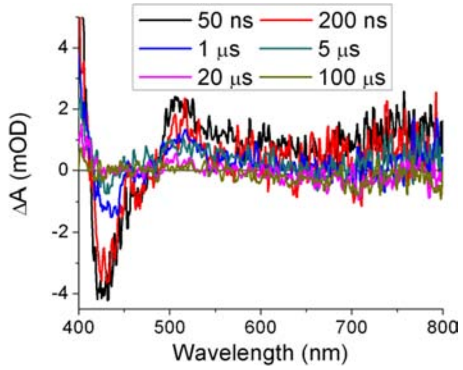

Figure 5. Transient absorption spectra after excitation of NiO thin films co-adsorbed with C343 and **1** with pulsed laser light (9 mJ cm^{-2}, 8 ns, 460 nm) results in the formation of **1**(−) and NiO(+) within 50 ns of excitation; recombination occurs on a 100 μs time scale.

atmosphere but without **1** co-adsorbed. After the excitation of C343 on NiO by itself, no signals were observed at our signal detection limit on a time scale of 50 ns or longer.

A plausible explanation for the observed formation of **1**(−) and NiO(+) from the excitation of C343 is presented in Scheme 1. As previously stated in the literature, excitation of

Scheme 1. Reduction of Complex 1 Co-adsorbed to NiO from the Selective Excitation of C343/NiO

$$C_{343}/NiO \xrightarrow{h\nu} C_{343}^{*}/NiO \tag{1}$$

$$C_{343}^{*}/NiO \longrightarrow C_{343}(-)/NiO(+) \tag{2}$$

$$C_{343}(-)/NiO(+) + \mathbf{1}/NiO \longrightarrow C_{343}/NiO(+) + \mathbf{1}(-)/NiO \tag{3}$$

$$C_{343}/NiO(+) + \mathbf{1}(-)/NiO \longrightarrow C_{343}/NiO + \mathbf{1}/NiO \tag{4}$$

C343 on NiO results in the formation of C343(−)/NiO(+) within femtoseconds of light absorption, (1) and (2) in Scheme 1.[14,15] In the absence of an accessible electron acceptor, recombination between C343(−) and NiO(+) occurs on the picosecond time scale.[14,15] Due to this rapid charge recombination, it has been previously proposed that charge transfer from C343(−) bound to NiO to electron acceptors requires pre-association between the electron acceptor and C343.[14,18] Based on the driving force (~500 mV), a bound C343(−) may directly reduce a neighboring bound complex **1**, (3) in Scheme 1.[11,13] The initial state is reset by interfacial charge recombination between **1**(−) and NiO(+), (4) in Scheme 1.

Due to the bulky phenyl groups at the phosphorus ligands, the iron center in **1** is relatively shielded from the surface of NiO. The slow recombination kinetics between **1**(−) and NiO(+) may be due in part to the large electron tunneling distance between the iron center and the NiO surface through five saturated bonds. It has been previously proposed that NiO holes have low charge mobility and are more localized than TiO_2 conduction band electrons.[16,17] To aid in the migration of electrons across the surface of NiO, a self-exchange mechanism between neighboring C343 molecules may be active on a sub-nanosecond time scale. This self-exchange mechanism has been previously observed in molecular stacks of perylene diimide.[19] If a self-exchange mechanism exists, then the true distance between **1**(−) and NiO(+) may be significantly larger due to the generation of charge carriers on C343/NiO sites non-adjacent to **1**/NiO sites. We propose that this may be one reason for the much slower recombination with NiO(+) from **1**(−) than from most reduced dyes investigated before.[14,15,18,20]

It is of note that the transient spectra in Figure 5 are similar to previously published spectra for the triplet excited state of C343 (^{3}C343).[15] However, the ^{3}C343 state has not been observed on the surface of NiO for longer than 2 ns,[15] the yield of ^{3}C343 is very small both on NiO and in solution,[14] the transient spectra that we measure are not observed in the absence of **1**, and we are unaware of any mechanism whereby **1** could *increase* the lifetime of the ^{3}C343 state. It is therefore highly unlikely that the C343 triplet state contributes to the observed spectral features.

In conclusion, we have observed charge recombination between singly reduced H_2-generating catalysts and valence band holes in NiO on the 100 μs time scale. From the transient absorption, we infer that the reduced form of **1** results from electron transfer from neighboring reduced C343 molecules, which were generated from the excitation of C343 photosensitizers bound to NiO and potentially in close contact with **1**. We believe this represents the first instance of "electron-hopping" between molecules along the surface of a semiconductor and the first evidence of reduction of a hydrogen-generating catalyst on the surface of NiO.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization of **1** and **2**; experimental details for sample preparation and measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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