



Direct Photoactivation of a Nickel-Based, Water-Reduction Photocathode by a Highly Conjugated Supramolecular Chromophore

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January 1, 2018

THE UNIVERSITY of North Carolina at Chapel Hill

DEPARTMENT OF CHEMISTRY

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Professor Alice Stevenson Publishing Editor Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, CB4 0WF, UK

Dear Alice:

We are submitting a revised version of the manuscript entitled "Direct Photoactivation of a Nickel-Based, Water-Reduction Photocathode by a Highly Conjugated Supramolecular Chromophore" for consideration in *Energy & Environmental Science*.

We have carefully considered the reviewers' comments. Their comments have been addressed with point-by-point responses, along with changes and additions made to the manuscript (highlighted throughout) and the supplementary information. Those responses are submitted as a separate file along with the revised manuscript.

Thank you for your consideration. We look forward to hearing from you.

Sincerly,

Tom

Thomas J. Meyer Professor of Chemistry University of North Carolina at Chapel Hill Referee: 1

Comments to the Author

B. Shan and co-workers present an experimental study of a composite electron donor/chromophore/catalyst (NiO/Zn-Mr complex/NiSx) which functions as a hydrogen evolution photocathode under illumination at 445 nm. Although this type of system has some conceptual resemblance to a DSSC, it differs crucially in that a hole from the molecular absorber is transferred to the mesoporous support, as opposed to an electron; the electron in the complex is thus available for driving reduction reactions in the electrolyte. A key claim of this work is the formation of a relatively long-lived redox-separated (RS) state. The electron in this state is able to reduce methyl viologen but not protons. However, deposition of a NiSx hydrogen evolution catalyst, apparently at the surface of the mesoporous stack (Fig. 1), allows proton reduction to occur with an overall quantum yield of about 1% (page S9). It is noted that a substantial fraction of the main text is devoted to describing how it was possible to electrodeposit the HE catalyst, as the NiO structure is quite insulating (Fig 3A). The characterization work is extensive and appropriate, and includes transient spectroscopy and the observation of ca. 100 microamp cm^-2 photocurrents under 10 mW cm^-2 of quasi-monochromatic illumination, which should be nearly fully absorbed by the dye at the wavelength employed, Fig. 2A.

There is a substantial amount of prior work with similar systems, as can be seen in the reviews which are refs. 13-16 in the present ms. The question then arises as to whether the system presented in an advance that meets the general interest criterion of EES. In my opinion it does not. The primary reason for saying this is the overall low QE, ca. 1%, which the authors mention only in the SI (but could be anticipated by the small photocurrents, particularly with well-absorbed monochromatic light). Also, the phrase "Water-Splitting Photocathode" in the title and elsewhere is misleading. The photocathode generated H2 with a QE of ~1% and an FE of ~75% with the O2 evolution, if it is occurring, being at the counter electrode. One can note the title of the Gibson review article (Chem. Soc. Rev. 2017) which uses the correct designation of "hydrogen evolution photocathodes" (n.b. correct language is used in synopsis accompanying the TOC graphic).

I would also observe that the "Broader Context" statement is basically a restatement of the Abstract and did not convince me regarding the broader impact of the work. That said, the work is highly suitable, with some revisions, for a more specialized journal. The high demonstrated stability of the system is a notable outcome, as well as the careful characterization.

<u>Author Response</u>: We thank the reviewer for the comments and suggestions. With regard to the photoelectrocatalytic efficiencies, the photocathode described here is more efficient than the previously reported dye-sensitized photocathodes with surface-immobilized dye and catalyst on metal oxide electrodes (reference: *Chem. Soc. Rev.*, **2017**, 46, 6194-6209). The objective of the current manuscript is to present a fundamentally new approach for designing photoelectrodes based on a long-lived, redox-separated excited state of a highly conjugated supramolecular chromophore. The excited state activates the electrodeposited catalyst directly for water reduction and injects holes to NiO, minimizing the loss of redox equivalents in the electron transfer scheme. The approach is important and would help guide future strategies to enhance the performances of photoelectrodes for water splitting or carbon dioxide reduction.

We agree with the reviewer that this photocathode in the 3-electrode setup only reduces water to hydrogen without oxygen evolution at the platinum anode. We have changed "water splitting" to "water reduction" in the title and the text.

We have changed the "Broader Context" and added the following text (highlighted) to emphasize the impact of this study on the field of dye-sensitized photoelectrosynthesis cells.

"Here, we present a new approach for the design of dye-sensitized photocathodes. It uses a highly conjugated supramolecular chromophore that forms a long-lived, redox-rich excited state for efficient catalyst activation and hole injection into NiO. The approach highlights the importance of excited state charge-separation dynamics for photoelectrocatalytic water reduction. The cell design could lead to a new class of photoelectrosynthesis cells that combine a wide range of semiconductors, photosensitizers and catalysts with aligned energetics for water splitting or carbon dioxide reduction."

Specific comments are as follows.

1. Abstract. "minimizes energy loss along the photoinduced electron transfer steps towards water splitting." As commented above, the system does not split water (as opposed to a particle-based photocatalyst).

Author Response: We have changed "water splitting" to "water reduction" in the text.

2. The Abstract does not mention the efficiency or make it clear why this is a major advance vs. prior art. The last sentence is about the method used to make the HE catalyst, for example. "which enables electrodeposition of the catalyst under negative bias and formation of the integrated photocathode."

<u>Author Response</u>: We agree that the abstract would be clearer with additional statements on the performance of the photocathode. The modified version includes the text highlighted in the abstract.

3. Broader context. "The photocathode shows an enhanced photoelectrocatalytic performance..." Enhanced compared to what? I saw no comparison to prior art.

<u>Author Response</u>: The term "enhanced efficiency" is referred to the comparison with known dyesensitized photocathodes with surface-immobilized dyes and catalysts on metal oxide electrodes (reference: *Chem. Soc. Rev.*, **2017**, 46, 6194-6209).

4. Reference 1 is a self-citation from nearly 20 years ago.

<u>Author Response</u>: Reference 1 is relevant in describing earlier homogeneous photosynthesis systems. With references 2-4, it cites earlier examples of chemical approaches for artificial photosynthesis.

5. Introduction. "In those systems, the overall efficiencies are usually downhill," What is a downhill efficiency?

Author Response: We have re-written that statement in the first paragraph on page 3 to:

"For those systems, the overall efficiencies decrease at each branching point along the electron transfer chains."

6. Figure 4. The photocurrent appears to be independent of bias over the range shown. At more positive potentials, does the photocurrent decrease?

<u>Author Response</u>: The photocurrent decreases significantly for the photocathode under bias more positive than 0.1 V vs NHE. We have added Figure S6 to show those changes. Related discussion has been added in the 2^{nd} paragraph on page 11.

"Diminished photocurrents were observed for the photocathode under bias more positive than 0.1 V vs NHE, Figure S6."

7. The pH dependence (not monotonic) would be made more clear with an inset in Fig 5B to show photocurrent vs. pH.

<u>Author Response</u>: An inset has been added in Fig. 5B to show the observed photocurrent densities at the 2^{nd} minute for the photocathodes in different pH buffers.

8. Page 15. "the photocurrents drop by a factor of \sim 2-4 due to the decreased catalyst activity at low proton concentrations." Are there measurements of the NiSx only to support this statement?

<u>Author Response</u>: We thank the reviewer for the suggestion. We have added Figure S7 to show the electrocatalytic performance of the photocathode at pH higher than 4.5. The following text (highlighted) has been added in the first paragraph on page 13.

"At pH 5.8 and 7.0, the photocurrents drop by a factor of ~2-4 due to the decreased catalyst activity at low proton concentrations, which is also shown by the electrocatalysis in Figure S7 for the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x at higher pH values."

9. Page 20, Conclusions. "and aqueous stability arising from its hydrophobic nature." This is the first mention of hydrophobicity.

<u>Author Response</u>: In the discussion of light absorption efficiency on page 7, we alluded to the surface-stability of the chromophore on NiO in aqueous solutions. The high stability is attributed to its strong hydrophobic nature. Related text has been highlighted on page 7.

"the considerably higher molar extinction coefficients of ZnPRu²⁺ and its strong hydrophobicity result in greater light absorption efficiency for it on NiO over extended periods in aqueous solutions. The stability was examined by immersing NiO|-ZnPRu²⁺ in pH 1, 4.5 and 7 buffer solutions and monitoring their UV-Vis absorption changes, which showed no sign of desorption or degradation of the dye for at least seven days." Referee: 2

Comments to the Author

This manuscript by Meyer and co-workers reported the construction of water-splitting photocathode sensitized by a supramolecular chromophore (ZnPRu2+) with surface-deposited NiMo0.05Sx as hydrogen-evolving catalyst. The topic of the present work is of significantly scientific interest, which could attract a broad readership to people working in solar energy conversion filed. Also, the manuscript is well-written and organized. Therefore, I would like to recommend its acceptance in Energy & Environmental Science after addressing the following concerns in the revised manuscript.

1) In page 13 of 32, the blue trace in Figure 4 indicates the LSV test under dark, please correct the writing in the text. Also, the authors may provide the data of NiO/-ZnPRu2+ electrode under intermittent irradiation for comparison.

<u>Author Response</u>: In Figure 4, the blue and orange traces show the LSV for NiO|-ZnPRu²⁺ and NiO|-ZnPRu²⁺ $|NiMo_{0.05}S_x$ under dark, respectively.

We agree with the reviewer about adding a control sample of $NiO|-ZnPRu^{2+}$ for photocurrent comparison in Figure 4. The data has been added shown as the pink trace in Figure 4, with the statements in the first paragraph on page 11, "In the absence of the catalyst, NiO|-ZnPRu²⁺ exhibits a negligible photocurrent response under the same conditions (pink trace in Figure 4)".

2) In page 14 of 32, what is the applied bias potential used in the experiments shown in Figure 5? If the applied bias potential is negative than -0.4 V vs NHE, there would be a considerable contribution to the detected current from electrocatalytic water reduction.

<u>Author Response</u>: The applied bias was -0.15 V vs NHE. We have added that information in the caption of Figure 5 and in the first paragraph on page 7.

3) Some of the photocurrent density curves shown in Figure 5 exhibit a sharp spike when the illumination light is on? But others do not have that behavior. The authors may provide a reasonable explanation to clarify such difference.

<u>Author Response</u>: We thank the reviewer for the suggestion. We have added the following text (highlighted) in the first paragraph on page 13 to discuss the changes in the initial spikes of those photocurrent responses.

"The traces in Figure 5 show a decrease in the initial spikes as the proton concentration was increased. At higher proton concentrations, the density of surface traps of NiO is reduced due to enhanced proton intercalation³³. The decreased spikes for the photocathode at low pH reveal less hole injection to those surface trap states."

4) In page 18 of 32, the phrase "0.42 V vs NHE" should be "-0.42 V vs NHE".

<u>Author Response</u>: We thank the reviewer for catching that typo. It has been corrected to "-0.42 V vs NHE".

Referee: 3

Comments to the Author

This manuscript by Tom Meyer and colleagues reports on an innovative type of photocathodes for H2 evolution that use a dye-sensitized NiO electrode coupled with a solid-state H2 evolution catalyst. To date such photocathodes are either fully inorganic (ie with both photoactive and catalytic solid state components) or fully molecular. The only example of such a construction concerns a photoanode for O2 evolution (ref 13) using Ru-based dyes and IrO2 catalyst.

The photocathode reported here is also the most performant reported so far in the literature. In addition, the authors thoroughly characterize their new system, including with original methods (EIS) so far not used in the field.

I therefore recommend publication in Energy Environ. Sci.

I think that the manuscript could be strengthened by a comparison with control photocathode architectures based on simple Zn-based or Ru-based chromophores.

<u>Author Response</u>: We agree with the reviewer that adding those control samples would strengthen the paper. We have added the photocurrent responses for the photocathodes sensitized by zinc^{II} porphyrin or ruthenium^{II} bis(terpyridine) coupled with the NiMo_{0.05}S_x catalyst, Figure S9. The resulting photocurrents are much smaller than that for the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x. Those examples point to the importance of the chromophore, ZnPRu²⁺, in the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x which greatly contributes to its photoelectrocatalytic performances.

Related discussion has been added in the second paragraph on page 13:

"Replacing ZnPRu²⁺ with the ruthenium^{II} bis-terpyridine $(Ru(tpy)_2^{2+})$ or the zinc porphyrin (ZnP) complex as the chromophore in the photocathode resulted in significantly decreased photocurrents as shown in Figure S9. Those results indicate that the efficiency of the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x is tied to the supramolecular chromophore, ZnPRu²⁺."

Also, it would be interesting to note the similarity in function with molecular photocathodes in which the HER catalyst is formed by reorganization of the NiO substrate (see the recent J Phys Chem C article from Spiccia and colleagues).

<u>Author Response</u>: We thank the reviewer for this suggestion. In the reference (*J. Phys. Chem. C* **2017**, 121, 25836-25846), the authors report that NiO nanoparticles that diffuse out of the NiO electrode (prepared from pre-formed NiO nanoparticles) serve as a pre-catalyst for hydrogen evolution from water. The actual catalyst (Ni⁰) forms following photoreduction of NiO nanoparticles by the reduced chromophore. As described, that mechanism relies on the presence of bare NiO particles that are not covered by any surface-bound molecules. In the present study, however, we derivatized the NiO electrode (prepared from a sol-gel precursor by using Ni²⁺ and F108 co-polymer) with a full surface coverage of the hydrophobic dye molecules, which precludes the possibility of diffusive NiO nanoparticles. In the absence of the catalyst, NiMo_{0.05}S_x, there was no hydrogen evolution, indicating that the actual catalyst in this photocathode is NiMo_{0.05}S_x.

Related text can be found in the first paragraph on page 11, "In the absence of the catalyst, NiO|-ZnPRu²⁺ exhibits a negligible photocurrent response under the same conditions (pink trace in Figure 4)", and in the second paragraph on page 13, "No hydrogen was produced in the absence of the chromophore or the catalyst.". "There is a substantial amount of prior work with similar systems, as can be seen in the reviews which are refs. 13-16 in the present ms. The question then arises as to whether the system presented in an advance that meets the general interest criterion of EES. I not " I do not agree with this statement. The authors report on a novel photocathode architecture combining a dye-sensitized electrode and a solid-state HER catalyst. The only example with such an architecture is a photoanode from the Mallouk group.

"The primary reason for saying this is the overall low QE, ca. 1%, which the authors mention only in the SI (but could be anticipated by the small photocurrents, particularly with well-absorbed monochromatic light)" While I can agree that this number is low, the performances reported here are the highest reported so far with NiO-based photocathode.

the phrase "Water-Splitting Photocathode" in the title and elsewhere is misleading. The photocathode generated H2 with a QE of \sim 1% and an FE of \sim 75% with the O2 evolution, if it is occurring, being at the counter electrode. One can note the title of the Gibson review article (Chev. Soc. Rev. 2017) which uses the correct designation of "hydrogen evolution photocathodes" (n.b. correct language is used in synopsis accompanying the TOC graphic)" I agree with such a statement.

<u>Author Response</u>: We agree with the reviewer that "water splitting" should be changed to "water reduction", since this photocathode produces hydrogen without oxygen evolution at the anode. We have made those changes as highlighted in the title and the text.

Direct Photoactivation of a Nickel-Based, Water-Reduction Photocathode by a Highly Conjugated Supramolecular Chromophore

Bing Shan,[†] Animesh Nayak,[†] Renato N. Sampaio, Michael S. Eberhart, Ludovic Troian-Gautier, M. Kyle Brennaman, Gerald J. Meyer and Thomas J. Meyer*

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ABSTRACT: In dye-sensitized photoelectrosynthesis cells, multi-step photoinduced electron transfer takes place to generate redox-separated (RS) states which activate catalysts for water splitting or carbon dioxide reduction. From photoexcitation of the chromophores to formation of the RS states, the solar energy initially stored at the chromophore excited states is reduced stepwise in a sequence of photoinduced electron transfer steps. We report here a water-reduction photocathode based on a supramolecular chromophore, an ethyne-bridged (porphyrinato)zinc^{II} and bis(terpyridyl)ruthenium^{II} complex, which is surface-bound to a mesoporous nickel oxide electrode, with an over-layer of nickel sulfide derivative as a water reduction catalyst. Visible light excitation of the chromophore generates a long-lived RS state that forms directly at its excited state with electron delocalized at the terpyridyl ligands for transferring to the nickel sulfide catalyst, and hole at the zinc porphyrin for injecting into the nickel oxide electrode. The resulting photocathode shows enhanced photoelectrocatalytic performances relative to the previously reported NiO-based photocathodes. A key element lies in the efficient, direct activation of the catalyst by the long-lived, RS excited state that minimizes the energy loss along the photoinduced electron transfer steps towards water reduction.

Broader context

Dye-sensitized photoelectrodes combining surface-immobilized catalysts for water splitting or CO₂ reduction present a promising strategy for solar fuel generation. To date, dye-sensitized photocathodes have shown much lower photoelectrocatalytic efficiencies relative to their anode counterparts, mainly due to rapid interfacial charge recombination and low quantum yields of photogenerated reducing equivalents. Adding redox mediators either on electrode surfaces or in electrolyte solutions can slow down the recombination and help to generate redox-separated states for delivering electrons to the catalysts. However, for those modified photocathodes, the quantum yields of reducing equivalents and the excited state energy are reduced along the multistep photoinduced electron transfer process, limiting the photoelectrocatalytic performances. Here, we present a new approach for the design of dye-sensitized photocathodes. It uses a highly conjugated supramolecular chromophore that forms a long-lived, redox-rich excited state for efficient catalyst activation and hole injection into NiO. The approach highlights the importance of excited state charge-separation dynamics for photoelectrocatalytic water reduction. The cell design could lead to a new class of photoelectrosynthesis cells that combine a wide range of semiconductors, photosensitizers and catalysts with aligned energetics for water splitting or carbon dioxide reduction.

INTRODUCTION

In artificial photosynthesis,¹⁻⁴ an important approach is the dye-sensitized photoelectrosynthesis cell which operates by integration of semiconductor p-n junctions, surface-bound photosensitizers and catalysts for solar fuel generation.⁵⁻⁹ In those systems, activation of the catalysts proceeds by redox equivalents that are separated from the semiconductor surfaces, through electron transfer at forward rates faster than the sum of the reverse rates. In order to slow down the reverse electron transfer and generate long-lived, redox-separated (RS) states for catalysts activation, the photoelectrodes are usually coupled with electron mediators in solutions,¹⁰⁻¹² or modified with surface-bound molecular donor-acceptor assemblies.¹³⁻¹⁶ For those systems, the overall efficiencies decrease at each branching point along the electron transfer chains.

For a dye-sensitized photoelectrosynthesis cell, the quantum yield of RS states for catalyst activation can potentially be increased by reducing the number of electron transfer steps towards generation of the RS states, since each electron transfer step is accompanied with a loss of efficiency. In that regard, a chromophore forming a long-lived, RS state initially at its excited state that transfers the photogenerated redox equivalents to a catalyst should be ideal for enhancing the overall photoelectrocatalytic performance.

We describe here a new water-reduction photocathode based on a highly conjugated supramolecular chromophore on NiO electrode with an over-layer of electrodeposited water reduction catalyst, molybdenum-doped NiS_x (NiMo_{0.05}S_x)¹⁷⁻¹⁹, as shown in Figure 1. The chromophore is an ethyne-bridged (porphyrinato)zinc^{II} and bis(terpyridyl)ruthenium^{II} complex (ZnPRu²⁺) which was prepared by metal-mediated cross-coupling of an ethyne-functionalized (porphyrinato)zinc^{II} intermediate with a halogenated derivative of bis(terpyridyl)ruthenium^{II}.^{20, 21} The structure of ZnPRu²⁺ contrasts with conventional covalently linked analogs by its rigid, highly π -conjugated ethyne-bridge which aligns the charge transfer dipole and induces efficient, intramolecular, excited-state electronic communication between the two subunits. The excited state is distinctive in its long-lived RS resonance structure with the electron and hole separated at the terpyridine and zinc porphyrin moieties, respectively. In the absence of a quencher, the RS excited state decays via slow charge recombination with a lifetime of several microseconds. In the integrated photocathode, it transfers the electron to the NiS_x catalyst and hole to the NiO electrode. Catalyst activation directly by the excited state with a long-lived RS feature minimizes

the loss of efficiency along the photoinduced electron transfer steps and significantly preserves the excited state energy for use in driving the catalytic reactions.



Figure 1. The structure (A) and cross-section scanning electron microscopic (SEM) image (B) of the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x.

METHODS

Materials. Nickel chloride hexahydrate, sodium molybdate dihydrate, thiourea, lithium perchlorate, tetrabutylammonium hexafluorophosphate (>99.0%), sodium acetate, acetic acid (>99.7%), Synperonic F-108, potassium chloride (\geq 99.5%), and methyl viologen dichloride were used as received from Sigma-Aldrich. Acetonitrile (Optima LC/MS) was purchased from Fisher Scientific. Distilled water was further purified with a Milli-Q Ultrapure water purification system (Milli-Q water). Fluorine-doped tin oxide (FTO; resistance 15 Ω /sq) glass was purchased from Hartford Glass Inc. and cut into 10 mm x 40 mm strips as substrates for coating with sol-gel Ni²⁺ paste. NMR were recorded in Bruker 400 MHz NMR instrument. Mass spectra were obtained by a FT-ICR (Thermo LTQ-FT-ICR-MS-7T) instrument equipped with electrospray ionization (ESI).

Synthesis of ZnPRu²⁺. The synthetic scheme is shown in Figure S1. The precursors, EPZnE and RuBr (structures in Figure S1), were synthesized by using the procedures published earlier.²² In a 100 mL Schlenk tube EPZnE (150 mg, 0.154 mmol) and RuBr (115 mg, 0.123 mmol) were

added with a stir bar. Trisdibenzylideneacetone dipalladium(0) (15 mg, 16.4 mol) and triphenylarsine (50 mg, 0.164 mmol) were added. A solvent mixture of dry THF (18 mL), CH₃CN (36 mL) and Et₃N (8 mL) was completely degassed by bubbling N₂ and added to the Schlenk tube. The reaction mixture was stirred under argon atmosphere at 55 °C for 16 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent of CH₃CN:H₂O:KNO₃ (aq) = 90:9:1. The major green-brown band (2nd green-brown band in the column) was collected and solvent evaporated. The residual dark brown solid was dissolved in a minimum volume of CH₃CN, excess ammonium hexafluorophosphate and H₂O were added. Dark brown precipitate of RuPZnE (structure in Figure S1) (106 mg, 56% yield based on RuBr) was collected by filtration. ¹H NMR (CD₃CN, 400 MHz): 9.98 (d, 2H), 9.61 (d, 2H), 9.40 (s, 2H), 8.97 (d, 2H), 8.81 (m, 6H), 8.56 (d, 2H), 8.49 (t, 1H), 8.07 (t, 2H), 7.98 (t, 2H), 7.85 (t, 2H), 7.58 (d, 2H), 7.45 (d, 2H), 7.25 (m, 8H), 4.51 (s, 1H), 4.03 (t, 8H), 0.85 (t, 8H), 0.21 (s, 36H), is shown in Figure S2.

In a 100 mL Schlenk tube RuPZnE (108 mg, 0.059 mmol) and 4-iodocarboxylic acid (29 mg, 0.118 mmol) were placed with a stir bar. Trisdibenzylideneacetone dipalladium(0) (15 mg, 16.4 μ mol) and triphenylarsine (50 mg, 0.164 mmol) were added. A solvent mixture of dry THF (18 mL), CH₃CN (36 mL) and Et₃N (8 mL) was completely degassed by bubbling N₂ and added to a Schlenk tube. The reaction mixture was stirred under argon atmosphere at 50 °C for 2 h. The reaction mixture was cooled to r.t. and the solvent evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent of CH₃CN:H₂O:KNO₃ (aq) = 90:9:1. The 2nd green-brown band was collected and solvent evaporated. The residual dark brown solid was dissolved in minimum volume of CH₃CN, excess ammonium hexafluorophosphate and H₂O were added. A dark brown precipitate of ZnPRu²⁺ (58 mg, 60% yield based on RuPZnE) was collected as a hexafluorophosphate salt by filtration. ¹H NMR (CD₃CN, 400 MHz): 9.96 (d, 2H), 9.69 (d, 2H), 9.40 (s, 2H), 8.56 (d, 2H), 8.48 (t, 1H), 8.25 (d, 2H), 8.18 (d, 2H), 8.06 (t, 2H), 7.97 (t, 2H), 7.85 (t, 2H), 7.58 (d, 2H), 7.45 (d, 2H), 7.23, (m, 8H), 4.02 (t, 8H), 0.85 (t, 8H), 0.22 (s, 36H), is shown in Figure S3. Mass (ESI-FTICR): 829.78 (z = 2), calculated mass for ZnPRu²⁺: 829.78.

Preparation of the photocathode. The mesoporous NiO was prepared according to the previous reports.^{23, 24} The thickness of NiO was measured as 1.8 μm by a Bruker Dektak XT

profilometer. The chromophore $ZnPRu^{2+}$ was loaded by immersing the NiO film in acetonitrile solution (0.5 mM) for 1 hour. The dyed NiO was then taken out of the loading solution and dried in air for another one hour. The NiMo_{0.05}S_x catalyst was deposited according to a modified, reported procedure¹⁷⁻¹⁹. A three-electrode cell with a Ag/AgCl reference electrode and a Pt mesh counter electrode was used for electrodeposition of the catalyst. Prior to applying bias, the deposition bath containing 50 mM NiCl₂, 2.1 mM Na₂MoO₄ and 1.0 M thiourea was degassed with N₂ for 30 min. Deposition of the catalyst was achieved through differential pulse amperometry with a CHI 660E potentiostat by applying a forward pulse bias at -1 V vs Ag/AgCl for 5s/pulse and a reverse pulse bias at 0.2 V vs Ag/AgCl for 5s/pulse. The forward and reverse pulses were cycled 15 times (except for the number of cycles dependent studies) for each deposition. The photocathode was taken out of the deposition bath immediately after deposition and rinsed with deionized water.

Electrochemical Characterization of ZnPRu²⁺. The cyclic voltammogram of ZnPRu²⁺ was acquired by scanning ZnPRu²⁺ in N₂ degassed acetonitrile solutions with 0.1 M tetrabutylammonium hexafluorophosphate. A typical three electrode cell was used with glassy carbon as working electrode, Ag/AgCl as reference electrode, and Pt mesh as counter electrode. Spectroelectrochemical measurements were carried out for ZnPRu²⁺ in acetonitrile solutions with 0.1 M tetrabutylammonium hexafluorophosphate. A Honeycomb quartz cell from Pine Research Instruments was used with a gold honeycomb working and counter electrodes and a Ag wire as a pseudo-reference electrode. Spectral changes were monitored with a HP 8453 Photodiode array. A CHI 660E potentiostat was used to control the applied potential at the honeycomb electrode.

Cross-Surface Electron Diffusion Coefficient. The apparent diffusion coefficient for $ZnPRu^{2+}$ on NiO was determined by chronoabsorptometry^{25, 26}. In a typical two-compartment three-electrode cell, the NiO | -ZnPRu²⁺ working electrode was immersed in 0.1 M LiClO₄ in N₂ degassed acetonitrile, with a Ag/AgCl reference electrode and a Pt mesh counter electrode in the other compartment. A forward bias at -0.8 V vs NHE was applied and maintained for 400 s, followed by a reverse bias at 0.1 V vs NHE for another 400 sec. Spectral changes were recorded with a HP 8453 Photodiode array at sampling rate of 1 s⁻¹. Absorptive changes from NiO background were subtracted.

Photoelectrocatalysis (PEC). A custom-made, two-compartment photoelectrochemical cell was used for photocurrent and H₂ evolution measurements. The cathode compartment was sealed

with a PEEK cap with ports for electrical connection to the photocathode, access for N₂-purging, and extraction of gas through a septum for H₂ quantification by gas chromatography. A CHI 601D potentiostat was used to supply the applied bias for the photocathode and record the current–time (i–t) signals. The photocathode active area (1 cm²) was immersed in a pH 4.5 buffer solution containing 0.1 M acetate. A bias at -0.15 V vs NHE was applied to the photocathode. Light illumination was provided by a solid-state light source (Lumencor, Inc.; λ_{max} : 445 nm, 20nm FWHM, output: 10 mW/cm²; beam diameter: 0.8 cm). The GC signal was calibrated with standard calibration gas (H₂ balanced in N₂) with a manufacturer reported linear response of the signal. The H₂ signal was also linearly converted to partial pressure for quantification of dissolved H₂ that was added to the amount of H₂ in the headspace for estimation of overall H₂ evolution.

Nanosecond Transient Absorption Spectroscopy (*ns***TA**). *ns***TA** measurements were performed with a nanosecond spectrophotometer as reported previously.²⁴ Single wavelength TA changes of the samples upon excitation by 532 nm laser pulses (2.0 mJ/pulse) were monitored by using a digital oscilloscope. Film samples with an area of 1.0 cm² were placed in a 1 cm pathlength quartz cuvette filled with pH 4.5 buffer solution containing 0.1 M acetate.

Electrochemical Impedance Spectroscopy (EIS). EIS measurements were carried out with a Gamry Reference 600 electrochemical impedance spectrometer at zero current condition by applying an AC voltage at 10 mV root-mean-square amplitude in a frequency range from 300 kHz to 1 Hz. The electrodes were immersed in deaerated pH 4.5 acetate buffer in the dark.

RESULTS AND DISCUSSION

Light Absorption Efficiency. The chromophore ZnPRu²⁺ exhibits broad light absorption in the visible region with high molar absorptivities, which translates to the high light absorption efficiencies in Figure 2(A) for ZnPRu²⁺ on a fully loaded NiO electrode. Based on the molar extinction coefficients in Figure 2(B), the surface coverage of ZnPRu²⁺ on NiO was estimated to be 18 nmol/cm², comparable to related porphyrin and ruthenium^{II} polypyridyl dyes with carboxylic/phosphoric acid anchoring groups on NiO. However, the considerably higher molar extinction coefficients of ZnPRu²⁺ and its strong hydrophobicity result in greater light absorption efficiency for it on NiO over extended periods in aqueous solutions. The stability was examined by immersing NiO|-ZnPRu²⁺ in pH 1, 4.5 and 7 buffer solutions and monitoring their UV-Vis absorption changes, which showed no sign of desorption or degradation of the dye for at least seven days.



Figure 2. (A) Fraction of light absorbed by $ZnPRu^{2+}$ on NiO from the inset absorption spectra of NiO | - $ZnPRu^{2+}$ (pink), NiO (gray) and $-ZnPRu^{2+}$ (blue); (B) Molar extinction coefficients (ϵ) of $ZnPRu^{2+}$ in acetonitrile.

Electron Percolation Assisted Catalyst Deposition. The water reduction catalyst, $NiMo_{0.05}S_x$,^{17-19, 27} was electrodeposited on NiO | -ZnPRu²⁺ by differential pulse amperometry (DPA) to give a porous nanoparticulate layer (surface SEM in Figure S4 (A)). The non-stoichiometric NiO is a p-type semiconductor due to the formation of Ni²⁺ vacancies and self-doping of Ni³⁺ ions in the presence of excess oxygen.^{28, 29} Under negative bias, NiO behaves as an insulator and blocks electron transport from the electrode to the external solution. For the electrodeposition of NiMo_{0.05}S_x, electrons were transported from the internal fluorine-doped tin oxide (FTO) substrate to ZnPRu²⁺ molecules directly attached to FTO, and further delivered through lateral electron hopping between adjacent ZnPRu²⁺ molecules, as illustrated in Figure

3(A). The applied bias passes the one electron reduction potential of $ZnPRu^{2+}$ (*vide infra*) for effective electrical conductivity in the supramolecular monolayer. In the structure, NiO is insulating but provides a mesoporous platform for supporting the supramolecular chromophore. The deposition components (Ni²⁺, Mo⁶⁺ and coordinated thiourea (TU)) were reduced by the electrons percolated over NiO surface through ZnPRu²⁺.

Cross-surface hole percolation has been observed for dye-sensitized TiO₂ photoanodes.^{25, 26,} ^{30, 31} The behavior is usually characterized by a sharp threshold below which the dye monolayer is not conductive due to a lack of percolation path to all the electro-active molecules. In our experiments, with complete surface loading of ~ 18 nmol/cm², the surface-bound ZnPRu²⁺ acts as a potential-controlled conductive monolayer for transporting electrons laterally across the surface by electron hopping. The apparent diffusion coefficient (Dapp) for characterizing the crosssurface charge percolation can be determined by chronoabsorptometry measurements²⁵ based on the classical chronocoulometric method. The results of a typical experiment are shown in Figure 3(B) with absorptive changes induced by the applied potential steps. Following a forward bias passing the reduction potential of ZnPRu²⁺ (vide infra), NiO|-ZnPRu²⁺ exhibits a bleach at ~470 nm. Based on a modified version of the Cottrell equation, D_{app} can be determined from the initial linear region of the resulting Anson plot³² (inset of Figure 3(B)) by using eq. 1. ΔA_f in eq. 1 is the estimated absorptive change based on the total electroactive molecules on electrode surface, as determined from linear extrapolation of the plateau region of the Anson plot. With the thickness of NiO (d = 1.8 μ m), D_{app} was estimated to be 1.4×10⁻⁹ cm²/s which translates to an electron hopping rate constant³⁰ (k_{hop} , eq. 2) of 0.15 s⁻¹.

$$D_{app} = \frac{\Delta A^2 \times d^2 \times \pi}{4\Delta A_f^2 \times t} \qquad \text{eq. 1}$$
$$k_{hop} = \frac{\pi^2 D_{app}}{4d^2} \qquad \text{eq. 2}$$

The value of k_{hop} for electron hopping is comparable to the values found earlier for hole hopping between surface-bond polypyridyl ruthenium^{II} complexes.³⁰ As noted above, such rapid electron hopping between adjacent ZnPRu²⁺ molecules provides a basis for effective electrical communication between the electrode and the deposition components that form the catalyst overlayer.



Figure 3. (A) Mechanism of electrodeposition of NiMo_{0.05}S_x on NiO | -ZnPRu²⁺ through electron percolation of ZnPRu²⁺ under negative bias; (B) absorptive changes of NiO | -ZnPRu²⁺ at 470 nm under a forward bias at -0.8 V vs NHE for 400 sec followed by a reverse bias at 0.1 V vs NHE, with the inset showing the optical Anson plot³²; (C) current from differential pulse amperometry (DPA) for electrodeposition of NiMo_{0.05}S_x under forward and reverse biases at -1 V and 0.2 V vs Ag/AgCl, respectively; (D) UV-Vis absorption spectra of NiO (1), NiO | -ZnPRu²⁺(2) and NiO | -ZnPRu²⁺ | NiMo_{0.05}S_x (3).

During electrodeposition of NiMo_{0.05}S_x, the deposition current increases with the deposition time, Figure 3(C). The increase is due to the continuous growth of NiMo_{0.05}S_x during the deposition cycles. The electrocatalytic performance of the photocathode NiO | - ZnPRu²⁺ | NiMo_{0.05}S_x was examined by linear sweep voltammograms (LSV), with results shown in Figure S5. In a pH 4.5 acetate buffer, the NiMo_{0.05}S_x deposited by 15 deposition cycles

performs the best relative to the others, with the highest catalytic current densities and least negative onset potential (-0.42 V vs NHE) for water reduction.

Photoelectrocatalysis (PEC). The photocathode, NiO|-ZnPRu²⁺|NiMo_{0.05}S_x, featuring high light absorption efficiency and stability in aqueous buffers, generates hydrogen from water upon visible light irradiation. Slow linear sweep voltammetry under intermittent illumination was used to characterize the photoelectrocatalytic performance. As shown in Figure 4, significant photocurrents over the irradiation intervals were generated under bias from -0.05 V to -0.40 V vs NHE. Diminished photocurrents were observed for the photocathode under bias more positive than 0.1 V vs NHE, Figure S6. The increase in dark current under bias past -0.40 V vs NHE was due to electrocatalytic water reduction. In the absence of the catalyst, NiO|-ZnPRu²⁺ exhibits a negligible photocurrent response under the same conditions (pink trace in Figure 4).



Figure 4. Linear sweep voltammograms (LSV) at 5 mV/s for NiO|-ZnPRu²⁺ (blue trace) and NiO|-ZnPRu²⁺|NiMo_{0.05}S_x (orange trace) under dark, and for NiO|-ZnPRu²⁺ (pink trace) and NiO|-ZnPRu²⁺|NiMo_{0.05}S_x (green trace) under intermittent irradiation (10 mW/cm² blue LED, 5 s/duration) in pH 4.5 acetate buffer.

The photoelectrocatalytic performance of the photocathode, NiO|-ZnPRu²⁺|NiMo_{0.05}S_x, is dependent on the deposition cycles of the catalyst and the proton concentration in the buffer medium. The plots in Figure 5(A) demonstrate the performance of the photocathodes with NiMo_{0.05}S_x from different deposition cycles. The highest photocurrents were obtained with the

15-cycle deposited catalyst layer (blue curve in Figure 5(A)), consistent with the electrocatalytic results. The decreased photocurrents for the samples prepared from \leq 15 deposition cycles are probably due to the limited number of catalytic active sites controlled by deposition cycles. For the samples with thicker catalyst layers prepared from \geq 20 deposition cycles, the electrons provided either electrochemically or photoelectrochemically may not be effectively transported to the active sites at the electrode/electrolyte interface, resulting in decreased photocurrents.



Figure 5. Photocurrent densities for NiO|-ZnPRu²⁺|NiMo_{0.05}S_x under intermittent irradiation (10 mW/cm² blue LED) and an applied bias of -0.15 V vs NHE, in pH 4.5 acetate buffer as a function of catalyst deposition cycles (A) and as a function of solution pH for the photocathode with the catalyst prepared from 15-cycle deposition (B). The inset in (B) shows the pH and the observed photocurrent densities (j_{photo}) at 2 min.

The photocathode also exhibits pH dependent behaviors as shown in Figure 5(B). In a range of pH buffers from pH 2.0 to 7.0, the photocathode at pH 4.5 gave the largest photocurrents. At pH 2.0 and 3.0, the dark currents are much larger. At pH 5.8 and 7.0, the photocurrents drop by a factor of ~2-4 due to the decreased catalyst activity at low proton concentrations, which is also shown by the electrocatalysis in Figure S7 for the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x at higher pH values. The traces in Figure 5 show a decrease in the initial spikes as the proton concentration was increased. At higher proton concentrations, the density of surface traps of NiO is reduced due to enhanced proton intercalation³³. The decreased spikes for the photocathode at low pH reveal less hole injection to those surface trap states.

During long-term PEC under optimum conditions (in pH 4.5 buffer, with catalyst from 15cycle deposition), the photocathode undergoes water reduction with persistent photocurrents shown in Figure S8. The produced hydrogen was quantified by gas chromatography, giving a Faradaic efficiency of $78.5\pm2.4\%$ over 2-hour PEC period. No hydrogen was produced in the absence of the chromophore or the catalyst. Replacing ZnPRu²⁺ with the ruthenium^{II} bisterpyridine (Ru(tpy)₂²⁺) or the zinc porphyrin (ZnP) complex as the chromophore in the photocathode resulted in significantly decreased photocurrents as shown in Figure S9. Those results indicate that the efficiency of the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x is tied to the supramolecular chromophore, ZnPRu²⁺.

Photoinduced Electron Transfer. In a dye-sensitized photoelectrosynthesis cell, the photoinduced electron transfer towards generation of RS state for catalyst activation is a key element that determines the cell efficiency. A significant contributor to the enhanced performance of NiO|-ZnPRu²⁺|NiMo_{0.05}S_x is the long-lived RS state²¹ of ZnPRu²⁺ which forms directly at its excited state. Since the triplet excited state (ZnPRu^{2+*}) does not exhibit stimulated emission, the lifetime of ZnPRu^{2+*} (τ_{es}) on an insulating mesoporous oxide, Al₂O₃, was estimated from nanosecond transient absorption (*ns*TA) of the excited state instead of emission spectroscopy for typical emissive (polypyridyl)ruthenium^{II} or (porphyrinato)zinc^{II} chromophores. As shown in Figure S10, following excitation at 532 nm, optical features of ZnPRu^{2+*} appear in the *ns*TA with ground state bleach bands at 440 nm and 680 nm and a positive absorption feature at ~560 nm. τ_{es} was determined to be ~6 µs from fitting of the time-resolved trace at 440 nm to biexponential or biphasic stretched exponential models²⁴, Figure S11. The *ns*TA results are

important in showing that ZnPRu²⁺* relaxes non-radiatively on a timescale much longer than the excited states of the two subunits, ZnP (~ 1.9 ns, S₁)^{34, 35} and Ru(tpy)₂²⁺ (~ 0.25 ns, ³MC)³⁶.

The *ns*TA for NiO | -ZnPRu²⁺ in Figure 6(A) shows the same features as that for Al₂O₃ | -ZnPRu²⁺ in Figure S10. Based on the spectroelectrochemical data of ZnPRu²⁺ in Figure 6(D), the absorptive features in Figure 6(A) arise from the excited state (ZnPRu^{2+*}) instead of the reduced dye (ZnPRu⁺). The decays of ZnPRu^{2+*} on NiO or Al₂O₃ are at the same timescale (Figure 6(B)). Those observations suggest that hole injection from the excited state to NiO does not occur.



Figure 6. (A) Nanosecond transient absorption (*ns*TA) spectra for NiO|–ZnPRu²⁺ in pH 4.5 acetate buffer; (B) time-resolved *ns*TA at 440 nm; (C) *ns*TA at 0.1 μ s for -ZnPRu²⁺ on Al₂O₃ (blue) and NiO (pink) in pH 4.5 acetate buffer, and for -ZnPRu²⁺ on NiO with 50 mM MVCl₂ in the solution (green); (D) molar

absorptivity changes of $ZnPRu^{3+}$ (pink), $ZnPRu^{+}$ (red) and $ZnPRu^{2+}$ * (blue) relative to $ZnPRu^{2+}$, and MV^{+} .

The triplet excited state of ZnPRu²⁺ (ZnPRu²⁺*) has the resonance structure, ZnP⁺Ru⁺, with the hole delocalized at ZnP (ZnP⁺) and the electron at the tpy ligands (tpy⁻).²⁰ The formal potentials of the two moieties, ZnP^{+/0} and tpy^{0/-}, were estimated from the cyclic voltammogram of ZnPRu²⁺ in Figure 7. Given the valence band potential of NiO (0.90 V vs NHE)³⁷ and the potential of ZnPRu^{3+/2+} (1.04 V vs NHE) that correlates to ZnP^{+/0} in the RS excited state (ZnP⁺Ru⁺), hole injection from the excited state into NiO valence band should be thermodynamically feasible. The inhibited injection observed for NiO|–ZnPRu²⁺* based on the *ns*TA spectra may result from the kinetically slower injection relative to the excited state relaxation. In Figure 7, ZnPRu²⁺ exhibits a quasi-reversible reduction wave at -0.76 V vs NHE for ZnPRu^{2+/+} that correlates with tpy^{0/-}. Based on the onset potential of the catalyst (-0.42 V vs NHE), reduction of the catalyst by tpy⁻ in the RS excited state is favored thermodynamically with a driving force of 0.34 eV.



Figure 7. Cyclic voltammogram of $ZnPRu^{2+}$ in N₂-degassed acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate.

In order to explore the electron transfer properties of the photocathode, nsTA experiments were carried out with methyl viologen (MV²⁺) as an external electron acceptor to substitute the catalyst in the photocathode. The nsTA spectrum shown as the green trace in Figure 6(C) for

NiO|-ZnPRu²⁺ with added MV²⁺ exhibits the absorption features of the oxidized dye (ZnPRu³⁺) and reduced methyl viologen (MV^{+.}) (molar absorptivities in Figure 6(D)). The *ns*TA spectrum indicates successful charge separation following photoexcitation of NiO|–ZnPRu²⁺ in the presence of the electron acceptor, NiO|-ZnPRu²⁺ + MV²⁺ \rightarrow NiO|-ZnPRu³⁺ + MV⁺. Since the formal potential of MV²⁺/ MV⁺ is -0.45 V vs NHE^{38, 39} which is near the onset potential of the NiMo_{0.05}S_x catalyst (-0.42 V vs NHE), the reduction of MV²⁺ by ZnPRu²⁺* can be regarded as the reductive activation of the catalyst with a similar driving force.

Comparisons of the *ns*TA spectra in Figure 6(C) reveal the sequence of light-induced electron transfer reactions for the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x, as shown in eq. 3-5. Upon light excitation, the RS state of the chromophore (ZnP⁺Ru⁺) forms at its triplet excited state, eq. 3. The catalyst is subsequently reduced by the long-lived, RS excited state, leaving the hole at ZnPRu³⁺, eq. 4. The initial state, ZnPRu²⁺, is regenerated following hole injection from ZnPRu³⁺ into NiO, eq. 5. The light-induced electron transfer steps are summarized below with the energy diagram shown in Figure 8.

$$NiO|-ZnPRu^{2+}|NiMo_{0.05}S_x \xrightarrow{HV} NiO|-ZnPRu^{2+}|NiMo_{0.05}S_x \leftrightarrow NiO|-ZnP^+Ru^+|NiMo_{0.05}S_x eq. 3$$

$$NiO|-ZnP^{+}Ru^{+}|NiMo_{0.05}S_{x} \rightarrow NiO|-ZnPRu^{3+}|NiMo_{0.05}S_{x}(e^{-})$$
 eq. 4

NiO|- ZnPRu³⁺|NiMo_{0.05}S_x(
$$e^{-}$$
) \rightarrow NiO(h^{+})|-ZnPRu²⁺|NiMo_{0.05}S_x(e^{-}) eq. 5



Figure 8. Energy diagram illustrating the light-induced electron transfer reactions in the photocathode $NiO|-ZnPRu^{2+}|NiMo_{0.05}S_x$. The grey dashed arrows represent the intra-molecular charge separation at the

excited state with the hole and electron separated at ZnP^+ and tpy^- moieties, respectively. Subsequent catalyst reduction by tpy^- and electron transfer from NiO to ZnP^+ are shown by the blue arrows.

Electrode Stability. Electrochemical Impedance Spectroscopy provides information on the charge transfer and transport kinetics at the electrode/electrolyte interface as well as the capacitive changes on the electrode.⁴⁰ To gain insight into the loss of photocurrent over 3-hour PEC, EIS was carried out for a fresh and a "degraded" photocathodes under zero current condition in the frequency range of 300 kHz to 1 Hz. The Nyquist plots for the photocathodes are shown in Figure 9, which were simulated by using the equivalent electrical circuit model in the inset. Each plot shows a semicircle at relatively high-frequency region and a straight line at low-frequency region. The ohmic series resistance (R_s) was determined in the high frequency region where the phase is zero, from the onset point of the semicircle. R_s for NiO | -ZnPRu²⁺ without the catalyst was applied during fitting for the other photocathodes with the catalyst (NiO | -ZnPRu²⁺ | NiMo_{0.05}S_x), with an additional resistance (R_{cata/dye}) included for the contact surface between the chromophore and catalyst. The charge transfer resistance (R_{ct}) at the catalyst/buffer interface was calculated by the radius of the semicircle.



Figure 9. Nyquist plots (scatter) with fits (lines) for NiO|-ZnPRu²⁺(blue), a fresh photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x (orange) and a photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x after 3-hour PEC (green). The inset shows the equivalent circuit model.

The fits of the Nyquist plots (lines in Figure 9) reveal that both the contact surface resistance ($R_{cata/dye}$) and charge transfer resistance (R_{ct}) increased for the photocathode after long-term PEC. The photocatalytic performance of the photocathode is presumably affected by several key factors of the catalyst, including surface area/morphology and electron/proton conductivity. The increase of $R_{cata/dye}$ and R_{ct} for the "degraded" photocathode implies that both the morphology and conductivity of the catalyst changed during long-term PEC. Proton intercalation ³³ appears not to play a role based on the EIS for the photocathode measured after immersion in pH 4.5 buffer for 3 hours in the dark, Figure S12.

CONCLUSION

We have described here a new water-reduction photocathode based on a supramolecular chromophore, an ethyne-bridged (porphyrinato)zinc^{II} and bis(terpyridyl)ruthenium^{II}, on NiO electrode with an over-layer of electrodeposited water reduction catalyst, Mo-doped NiS_x. Key features of the chromophore in the photocathode include its high molar absorptivity in the visible and aqueous stability arising from its hydrophobic nature. Formation of the integrated photocathode with the electrodeposited catalyst relies on the rapid cross-surface electron percolation in the chromophore provides a thermodynamic basis for reductive activation of the catalyst and hole injection into NiO. The enhanced efficiency of the photoelectrode is due in large part to the direct catalyst activation by the long-lived, RS excited state, which minimizes the energy loss along the simplified photoinduced electron transfer steps.

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Supplementary Information

Direct Photoactivation of a Nickel-Based, Water-Reduction Photocathode by a Highly Conjugated Supramolecular Chromophore

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Figure S1. Simplified scheme for the synthetic procedure of $ZnPRu^{2+}$.



Figure S2. ¹H NMR (400 MHz) of RuPZnE in CD₃CN.



Figure S3. ¹H NMR (400 MHz) of ZnPRu²⁺ in CD₃CN.







Figure S5. Linear sweep voltammograms of NiO|-ZnPRu²⁺|NiMo_{0.05}S_x with the catalyst from various DPA cycles in pH 4.5 acetate buffer.



Figure S6. Linear sweep voltammograms for NiO|-ZnPRu²⁺|NiMo_{0.05}S_x under dark (orange trace) or illumination (10 mW/cm² blue LED) (blue trace) in pH 4.5 acetate buffer. Scan rate: 5 mV/s.



Figure S7. Linear sweep voltammograms of NiO|-ZnPRu²⁺|NiMo_{0.05}S_x with the catalyst from 15-cycle DPA in pH 4.5-7.0 buffers.



Figure S8. Photocurrents $(j/\mu A \text{ cm}^{-2})$ showing long-term photoelectrocatalysis by the photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x with catalyst form 15-cycle DPA and in pH 4.5 acetate buffer with an applied bias of -0.05 V vs NHE.



Figure S9. Photocurrents for NiO $|-Ru(tpy)_2^{2^+}|NiMo_{0.05}S_x$ (red curve) and NiO $|-ZnP|NiMo_{0.05}S_x$ (blue curve) in pH 4.5 acetate buffer with an applied bias of -0.05 V vs NHE.



Figure S10. Nanosecond transient absorption (*ns*TA) following excitation of $Al_2O_3|$ –ZnPRu²⁺ at 532 nm as a function of time delay after the laser pulses. Solution medium: N₂ degassed pH 4.5 acetate buffer.



Figure S11. Time-resolved *ns*TA at 440 nm following excitation of $Al_2O_3|$ –ZnPRu²⁺ at 532 nm (blue, solid), biexponential fit (red, dashed) and biphasic stretched exponential fit (black, dashed). Solution medium: N₂ degassed pH 4.5 acetate buffer (aq., 0.1 M).



Figure S12. Nyquist plots for a photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x after immersion in pH 4.5 buffer for 3 hours in the dark (pink) and a photocathode NiO|-ZnPRu²⁺|NiMo_{0.05}S_x after 3-hour PEC (green). Comparison of the Nyquist plots indicates that proton intercalation is not a main cause for the increased resistance in charge transfer and contact surface of the "degraded" photocathode.

Faradaic Efficiency and Quantum Yield of Hydrogen Calculation.

The Faradaic efficiency was determined by the equation, Faradaic efficiency = $\frac{\text{mols of H}_2 \times 2}{\text{moles of electrons}}$. Based on the photocurrent results in Figure S6 and the quantification of hydrogen evolution from Gas Chromatography measurements, the Faradaic efficiency was determined to be 78.5±2.4% over 2-hour period of photoelectrocatalysis.

The quantum yield of hydrogen was determined to be 1.29±0.04%, according to the equation,

 $\eta_{QY} = \frac{n(H_2) \times N_A \times h \times c \times 2}{\lambda \times t \times I \times A}$, with n(H₂): moles of H₂ (moles), N_A: Avogadro constant (6.02×10²³ mol⁻¹), h: Planck constant (6.63×10⁻³⁴ kg m² s⁻¹), c: speed of light (3.0×10⁸ m s⁻¹), λ : wavelength (4.45×10⁻⁷ m), t: irradiation time (s), I: light intensity (0.01 W m⁻²) and A: irradiated area (1.0 m²).

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TOC: Control of photoinduced electron transfer flow in a NiO/Dye/NiS_x:Mo photocathode by a highly conjugated supramolecular chromophore for light-driven water reduction.