

DISSERTATION

INVESTIGATION INTO CATALYST INTERACTIONS IN A DYE-SENSITIZED
PHOTOELECTROCHEMICAL CELL FOR WATER OXIDATION CATALYSIS

Submitted by

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ABSTRACT

INVESTIGATION INTO CATALYST INTERACTIONS IN A DYE-SENSITIZED PHOTOELECTROCHEMICAL CELL FOR WATER OXIDATION CATALYSIS

Solar energy has the potential to contribute significantly to solving the global energy crisis. However, solar energy is both diffuse and intermittent, meaning the capture and storage of this energy is critical. One method of storing this energy is the generation of storable hydrogen fuel via photoelectrochemical water-splitting, that is, storing energy in chemical bonds, specifically the H-H bond. However, the efficiency of the water-splitting process is limited by the water oxidation reaction, a four-electron process occurring at the anode. As such, water splitting devices, and more specifically water-oxidation devices, have been the focus of research for several decades. One such strategy, employed herein, uses molecular light-harvesting dyes and associated materials to capture and convert energy from the sun into chemical bonds.

The work presented in this dissertation examines one such water-oxidation dye-sensitized photoelectrochemical cell (DS-PEC) with the goal of better understanding how charge-carrier interactions in the system are impacted by varying the system's catalyst, architecture and device composition. Throughout this dissertation a photoanode consisting of nanostructured SnO₂ coated in perylene diimide dye *N,N'*-bis(phosphonomethyl)-3,4,9,10-perylenediimide plus photoelectrochemically deposited cobalt oxide (CoO_x) is examined. Chapter I provides an in-depth overview to water-oxidation catalysis with a focus on the state of DS-PECs in the literature. Chapter II looks to understand the impact of an alumina overlayer on this DS-PEC system, with the specific goal of better understanding why the addition of the CoO_x catalyst decreases

photocurrent and increases recombination, a so-called “anti-catalyst” effect. The studies presented in Chapter II demonstrate that the presence of an ultrathin alumina overlayer by atomic layer deposition (ALD) increases photocurrents and decreases recombination in the device, although the addition of CoO_x catalyst still decreases photocurrent. Chapter III examines the same system with the continued goal of identifying the source of increased recombination and decreased photocurrents with CoO_x catalyst addition. Through a series of controls, residual carbon attributable to organic stabilizer used in the nanostructured SnO_2 synthesis is discovered to be the culprit of this “anti-catalysis” effect. Anodes made using more carbon-free SnO_2 deposited by ALD, rather than the nanostructured SnO_2 with residual carbon, show an increase in photocurrents with CoO_x addition. Subsequently, Chapter IV looks at two methods of overcoming and outcompeting the recombination attributable to residual carbon in the device. The effect of the residual carbon is shown to be mitigated through both the use of a more active iridium-based catalyst, amorphous Li-IrO_x , rather than CoO_x , and then through the use of a more carbon-free ALD- SnO_2 , without organic stabilizer, rather than nanostructured SnO_2 . The planar ALD- SnO_2 is compared to the nanostructured SnO_2 both on a per dye basis and on an electrochemically active surface area basis. The results presented in this dissertation offer fundamental insights into achieving both a better understanding, and an improved performance, of DS-PECs for water-oxidation catalysis that is a critical component of solar energy capture and storage.

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TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENTS.....	iv
I. INTRODUCTION.....	1
REFERENCES.....	15
II. ULTRATHIN ALUMINA PASSIVATION FOR IMPROVED PHOTOELECTROCHEMICAL WATER OXIDATION CATALYSIS OF TIN OXIDE SENSITIZED BY A PHOSPHONATE-FUNCTIONALIZED PERYLENE DIIMIDE FIRST WITHOUT, AND THEN WITH, COBALT OXIDE.....	23
Overview.....	23
2.1. Introduction.....	24
2.2. Experimental.....	28
2.3. Results and Discussion.....	32
2.4. Conclusions.....	49
REFERENCES.....	51
III. UNDERSTANDING THE “ANTI-CATALYST” EFFECT WITH ADDED COO _x WATER OXIDATION CATALYST IN DYE-SENSITIZED PHOTOELECTROLYSIS CELLS: CARBON IMPURITIES IN NANOSTRUCTURED SNO ₂ ARE THE CULPRIT.....	56
Overview.....	56
3.1. Introduction.....	57
3.2. Experimental.....	64
3.3. Results and Discussion.....	69
3.4. Conclusions.....	85
REFERENCES.....	87
IV. TWO METHODS OF OVERCOMING RESIDUAL CARBON-INDUCED RECOMBINATION IN A WATER-OXIDATION CATALYSIS DEVICE: EMPLOYING AN IMPROVED CATALYST, REDUCING THE RESIDUAL CARBON, AND QUANTITATING THE RESULTANT IMPROVED DEVICE.....	92
Overview.....	92
4.1. Introduction.....	93
4.2. Experimental.....	96
4.3. Results and Discussion.....	101
4.4. Conclusions.....	115
REFERENCES.....	118
V.SUMMARY.....	123
REFERENCES.....	131

APPENDIX I. SUPPORTING INFORMATION FOR CHAPTER II.....	133
REFERENCES.....	144
APPENDIX II. SUPPORTING INFORMATION FOR CHAPTER III.....	145
REFERENCES.....	158
APPENDIX III. SUPPORTING INFORMATION FOR CHAPTER IV.....	160
REFERENCES.....	166
LIST OF ABBREVIATIONS.....	167

I. INTRODUCTION

This dissertation follows a “journal’s format”, where each chapter has been prepared as a manuscript for submission and publication in a peer-reviewed chemistry journal. As such, each chapter follows the formatting guidelines of the respective journal. An overview is presented at the beginning of each chapter along with a footnote describing the specific contributions from potential co-authors. Chapters II, III, and IV have an accompanying Appendix that contains that Supporting Information from that chapter’s published paper, assembled at the end of the dissertation according to the graduate school’s format.

This introduction section consists of a background summary on water splitting, a brief outline of the state of the water-oxidation field, and a synopsis of the literature basis for the work herein, followed by a brief description of each chapter. Additionally, each chapter contains its own introduction to the specific area relevant to the research presented in that chapter.

Sustainably meeting humanity’s ever growing energy demand is one of the most significant scientific challenges of our time.¹⁻³ The collection and conversion of solar energy into storable energy is one viable approach towards meeting this challenge. However solar energy is diffuse, and the diurnal cycle of the sun means that solar energy is not always available. Hence, sustainable collection and storage of solar energy is necessary to make solar a viable renewable-energy option. One method of storing energy from the sun makes use of photoelectrochemical solar water splitting, which uses the energy from the sun to convert water into a storable fuel in the form of the chemical bond in H₂. The energy stored in the chemical bond of H₂ can then be released as either heat via combustion with O₂ or as electricity via a fuel cell.^{2,4,5}

The water splitting reaction occurs via two half reactions: the hydrogen-evolving reaction (HER) and the oxygen-evolving reaction (OER), which occur at the anode and cathode, respectively, Figure 1.1 and Figure 1.2. The goal of photoelectrochemical water splitting is to drive this electrochemical reaction using energy from the sun.

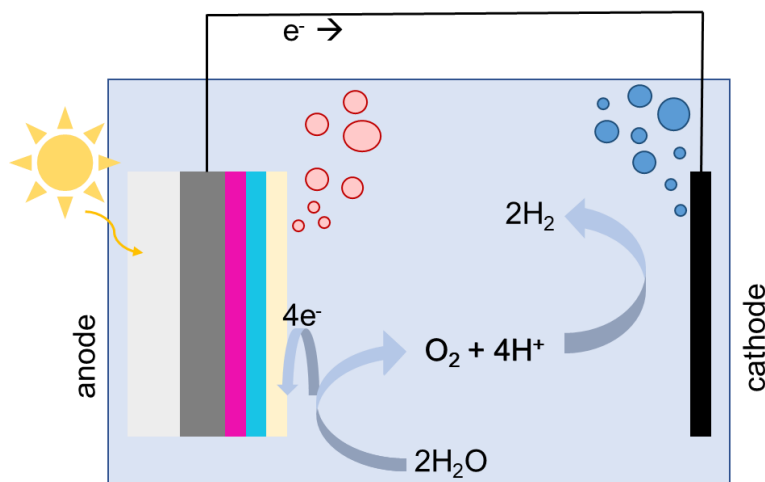
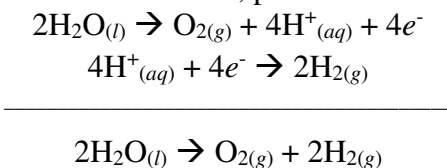


Figure 1.1. Illustration of water splitting reaction's two half reactions. The four-electron water oxidation half reaction occurs at the anode. Hydronium ions (H_3O^+ , shown as H^+ here for simplicity) and the electrons formed during water oxidation are then used to form storable hydrogen fuel at the cathode.

Figure 1.2. Balanced equations for water oxidation, proton reduction, and overall water splitting.



The OER, occurring at the anode, is the kinetic bottleneck of this reaction as it is a difficult four electron process.^{6,7} As such, study of the OER, and thus the photoanode, is critical to the development of a viable water-splitting device. In order to achieve significant reaction rates an overpotential, often ≥ 400 mV beyond the 1.23 eV thermodynamic requirement, is needed to overcome electron-hole recombination in these multi-electron reactions, even in the presence of efficient water oxidation catalysts (WOCatalysts).^{7,8} As such, there is significant interest in

understanding the source of electron-hole recombination reactions in water oxidation devices in order to minimize losses in efficiency. Realistically, solar-hydrogen efficiencies must be above 10% for practical commercialization and cannot be limited by use of expensive materials or issues with device stability—ideally producing H₂ gas competitive in price with natural gas.^{9,10}

Light-driven water splitting has been achieved by many researchers across many different device architectures and materials with varying degrees of complexity.^{11–15} For simplicity, three distinct architectures are briefly discussed herein. First, one method of light-driven solar water splitting involves the use of a simple p–n junction photovoltaic (PV) device wired to a commercial electrolyzer.^{9,16–19} These devices are often extremely expensive as they include rare elements and involve significant amounts of wiring between PV cells to an electrolyzer to achieve sufficient voltage. A second method of achieving solar water oxidation makes use of the suspension of a photocatalytic colloid, where water splitting occurs throughout the solution at the semiconductor–liquid junction on each particle’s surface.^{20–25} This second method is still comparatively new and is in early stages of research. There is also significant safety concern involved in the generation of both O₂ and H₂ in the same compartment. A third architecture uses integrated photoelectrochemical cells (PEC), where the light-collecting panel is submerged directly in aqueous solution to perform water oxidation directly on the device surface.^{6,7,26,27} Herein, we will focus on the third device design as it avoids the extensive costs associated with PV-electrolyzers and avoids the safety issues inherent in O₂ and H₂ co-generation systems.

Integrated PEC devices have taken many forms and have made use of a wide variety of materials. Most simply, an n-type photoanode or a p-type photocathode is submerged in an electrolyte solution, resulting a disparate Fermi level across the interface.⁶ To equilibrate, charge moves across the interface, depleting the area of the majority charge-carriers, resulting in the

formation of a space charge layer within the semiconductor near the interface.²⁸ An electric field is formed in this region, which impacts the movement of charge in the area and is often drawn as band bending at the semiconductor-liquid interface, Figure 1.3.^{7,28–30} This process and the subsequent band bending aid the transfer and separation of the photogenerated electrons and holes.³¹ For the purposes of water oxidation catalysis, illumination of this device results in the production of excited, photo-generated holes in the valence band, which then move towards the semiconductor-liquid interface, inducing oxidation reactions. The corresponding electrons in the conduction band migrate towards the bulk semiconductor (outside the band bending region) where they can be used to drive another reaction, like the HER, at a separate electrode.

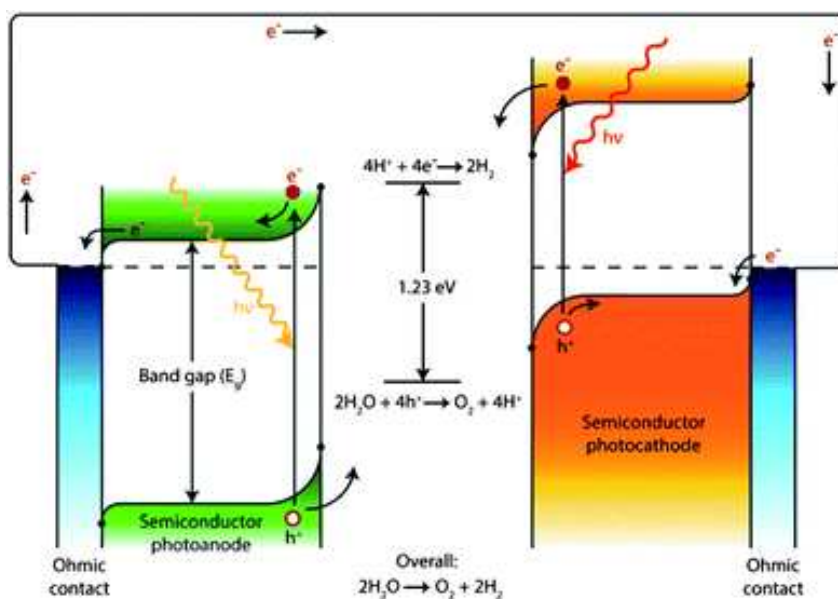


Figure 1.3. Band structure illustration of a photoanode and photocathode water splitting device after illumination, $h\nu$. Photon absorption, band bend of the semiconductors, charge separation, and both the HER and OER are shown. Figure adapted with permission from reference 10. Copyright 2013 Royal Society of Chemistry.

However, achieving water oxidation with only a single semiconductor requires a large band gap energy (ca. ≥ 1.6 eV to provide sufficient overpotential), the conduction and valence bands must be positioned appropriately to drive the water splitting half reactions, and the semiconductor

must be robust enough to withstand photo-corrosion. This results in a very limited selection of semiconductors that can be used alone for water oxidation, all of which have large (≥ 3.4 eV) band gaps, resulting in poor light absorption.²⁷

One strategy to improve PECs is the incorporation of a dye sensitizer, resulting in a dye-sensitized photoelectrolysis cell (DS-PEC). The DS-PEC architecture will be the focus of research presented in this dissertation. DS-PECs add a layer of dye molecules on the semiconductor surface to absorb visible light that is then followed by a rapid charge-transfer from the photoexcited dye to the semiconductor. DS-PEC devices are of significant interest as they provide increased light absorption with the addition of a near-monolayer of dye on the large semiconductor surface area while also maintaining a short exciton (coulombically bound electron–hole pair) diffusion length across the dye. Generally speaking, a DS-PEC consists of a minimum of three parts: a sintered nanostructured metal-oxide used both for charge transport and to increase surface area, a molecular light absorber, generally a monolayer of dye, and a photocatalyst for water oxidation. As one might expect, many reviews have been written on the topic of DS-PECs.^{7,32–37}

DS-PECs are made using sintered metal-oxide (M_xO_y) nanoparticle films with conduction bands at a potential such that sufficient driving force for efficient electron injection from the excited state of a molecular sensitizer to the conduction band occurs. Currently, a variety of metal-oxide films are used across DS-PEC devices, with TiO_2 being the most common but SnO_2 and WO_3 also frequently used.^{32–34,38} The identity of the metal-oxide used is known to alter the rate of electron injection and recombination, resulting in interest in different metal-oxides as well as different DS-PEC device formulations.^{39,40} Because nanostructured M_xO_y films are used widely across the DS-PEC literature, there are many different M_xO_y paste formulations and film preparations designed to yield reproducible films of optimized thicknesses, nanoparticle sizes, and

composition for specific systems.³⁹⁻⁴⁸ Research into oxygen vacancies in these M_xO_y films has been carried out, with evidence being found that the concentration of oxygen-vacancies can dictate which charge transfer pathways are most favorable.⁴⁹ Many of these nano- M_xO_y film syntheses rely heavily on organic molecules as stabilizers, thickeners, and to increase adhesion to the conductive glass.^{39,40,42,45,47,48,50} In discussions of optimal metal-oxides and discussions of device performance, *these organic components are not typically considered, as the films are often annealed, which is thought to remove the carbon.*^{42,51} However, often carbon still remains in the films, detectable by various methods by several groups.^{49,52} Hence, the possible implications of residual carbon in M_xO_y films in DS-PECs is of great interest and is the focus of the research presented in Chapter III.

Current best practices for comparing DS-PEC photoanodes are not standardized and rely heavily on steady-state photocurrent density and Faradaic efficiency for water oxidation. Of note, collecting and measuring oxygen generation can be very difficult and, hence, is still not widely reported in the literature despite being a critical metric of WOC. Additionally, steady-state photocurrents can be impacted by many variables beyond the main components used including the type of illumination (with several metrics being used regularly throughout the literature), the pH at which the photochemistry is run (as the thermodynamics of water splitting change significantly with pH), and the applied voltage at which the photocurrent density is measured, to name a few important variables. As such, comparisons across devices and systems are nontrivial and require scrutiny. Furthermore, judging / understanding device improvement can be difficult, as balancing elemental scarcity with device performance are often opposing considerations. Additionally, scalability and complexity in manufacturing of water oxidation devices, not simply Faradaic

efficiencies and photocurrent, are other factors that must be considered in determining if true device improvement has occurred.

Comparisons between devices should also include consideration of reproducibility, though many publications fail to discuss how reproducible their results are—or even if they have tested multiple, separately manufactured devices.^{53–56} Inherent in the DS-PEC field is some degree of artisanal, expert craftsmanship, resulting in photoactivities that may require specific skilled individuals to make the device, meaning peak performances may not be achievable in every replicate. Hence, reproducibility is of the utmost importance and needs to be a part of experimental design and reporting. Reproducibility is used incorrectly in the DS-PEC literature to describe the results of repeated experiments *on the same anode*, data which are better described by lifetime analysis than reproducibility.⁵⁷ Additionally, researchers often claim results are representative without showing error bars or detailing how many separate samples were tested.⁵⁸ Even in instances where multiple individual devices are made and tested, the average value without any error is presented.⁵⁹ Some researchers have already begun the shift towards reporting an average value of a minimum of three separately prepared and tested anodes *with* error.^{60,61} This is crucial to developing a robust understanding of the true, representative value of a given system, not simply a top performing anode selected (“cherry picked”) from a variety of mixed results.

The inclusion of reproducibility data is of immense importance as some techniques used in DS-PEC production are already known to be irreproducible.⁶² Moreover, the scaling up and manufacturing of already irreproducible devices is expected to be problematic if not near impossible. Understanding the true degree of variability in device performance is, then, a key to optimizing and improving state-of the art devices.

Many of these best-performing DS-PEC systems use rare-elements as catalysts and dyes, meaning in turn that they have limited potential commercial viability. Rare elements are not only expensive, but quantities are limited meaning that a reliance on such rare elements is not sustainable. Current state-of-the-art DS-PECs often use ruthenium and iridium catalysts to achieve the highest photocurrents in the field.^{7,39,41,59,61,63–76} However, to our knowledge, there are still no DS-PEC devices capable of achieving sufficient photovoltages to perform water splitting without the addition of applied bias even using the best rare element catalysts.

The current best-performing (i.e., highest reported steady-state photocurrent) devices have achieved photocurrents on the order of 400 $\mu\text{A}/\text{cm}^2$ at +0.4 V versus NHE⁷⁶ and 300 $\mu\text{A}/\text{cm}^2$ at +0.36 V versus NHE⁵⁹ using ruthenium-based catalysts. Research has begun to shift towards water splitting devices made *entirely* of inexpensive, earth-abundant materials, including both the catalyst and dye, though there are still significantly fewer of these systems being studied.^{42,50,77–80} However, as the “best” (i.e., possibly more efficient and quicker at charge collection and transfer) WOCatalysts currently in use are made of these expensive, rare elements, all earth abundant systems are often limited by device inefficiencies and recombination. Table 1.1, modified from Chapter IV, highlights the top performing DS-PEC devices and the top *all earth-abundant* DS-PECs, in their chronological order of appearance in the literature.

Table 1.1. Relative photocurrents for selected DS-PEC water oxidation systems using both earth-abundant and non-earth abundant catalysts. Adapted from Chapter IV.

Paper	Water Oxidation Catalyst	Dye	Scaffolding	Photocurrent	Light Source	All Earth Abundant System?
Sun and coworkers, 2015⁵⁹	Ru-pdc	D-A	TiO ₂	300 $\mu\text{A}/\text{cm}^2$ at +0.36 V vs NHE, pH 7	100 mW cm^2 , $\lambda > 400$ nm	No
Bignozzi and coworkers, 2015³⁹	IrO ₂	perylene bisimide	WO ₃	70 $\mu\text{A}/\text{cm}^2$ at +0.30 V vs NHE, pH 3	AM 1.5G, $\lambda > 450$ nm	No
Finke and coworkers, 2017⁴²	CoO _x	PMPDI	nano-SnO ₂	20 $\mu\text{A}/\text{cm}^2$ at +0.4 V vs NHE, pH 7	AM1.5 G	Yes
Meyer and coworkers, 2017⁷⁶	Ru(bda)	D- π -A	TiO ₂ /Al ₂ O ₃ core-shell	400 $\mu\text{A}/\text{cm}^2$ at +0.4 V vs NHE, pH 4.8	100 mW cm^2 , $\lambda > 400$ nm	No
Karadas and coworkers, 2020⁸¹	Prussian blue analog	Janus green B	Rutile TiO ₂	50 $\mu\text{A}/\text{cm}^2$ at +0.8 V vs NHE, pH 7	100 mW cm^2 , $\lambda > 420$ nm	Yes
Meyer and coworkers, 2022⁸⁰	CoF	D- π -A	TiO ₂	120 $\mu\text{A}/\text{cm}^2$ at +0.6 V vs. NHE), pH 7	100 mW cm^2 , $\lambda > 400$ nm	Yes

The work in the present dissertation focuses on understanding the all earth-abundant system described below.^{42,50,77} All earth-abundant devices are still uncommon in the DS-PEC literature, though recently published work has begun to develop WOCatalysts that reach the same order of magnitude of photocurrent as their rare element-based catalyst counterparts.⁸⁰ Recent work by the Meyer group showed photocurrents on the order of 120 $\mu\text{A}/\text{cm}^2$ at +0.6 V versus NHE using a device free from rare-element metals.⁸⁰ Briefly, photoanodes were made by co-loading a triphenylamine organic dye and a cobalt cubic catalyst on a TiO₂ thin film, resulting in a device that can perform water oxidation with 77% efficiency. This system is so successful because charge recombination is intentionally minimized in the device. Meyer and coworkers experimentally

tested dyes to find a dye that reduces recombination, with a dye containing a pH-insensitive pyridyl anchor that is thought to inhibit interfacial recombination performing the best. Using a molecular-catalyst-based, noble-metal free, dye-sensitized photoanode Meyers and coworkers suggest a path forward for the research of low-cost, efficient, earth abundant DS-PECs for water oxidation catalysis. More importantly, their work emphasizes the significance of understanding recombination in one's system and working to mitigate it.

Herein, my Ph.D. research seeks to understand and mitigate the problem of recombination in our DS-PEC photoanode system. The photoanode device of specific interest consists of nanostructured SnO_2 coated in a perylene diimide dye, *N,N'*-bis(phosphonomethyl)-3,4,9,10-perylenediimide (PMPDI, Figure 1.4), plus photoelectrochemically deposited cobalt oxide (CoO_x).^{42,50,77} Perylene diimide (PDI) dyes, such as PMPDI, are promising organic molecules for water oxidation catalysis as they strongly absorb visible light and are robust—basically a key component of Ferrari red car paint.⁸² PDIs are also relatively cheap, exhibit high thermal stability (300-600 °C),⁸³ and high oxidative stability in both air and water,⁸⁴ making them an ideal candidate for use in water-oxidation devices. These properties together have led to the use and study of PDI derivatives by several groups across several WOC systems.^{13,85–91}

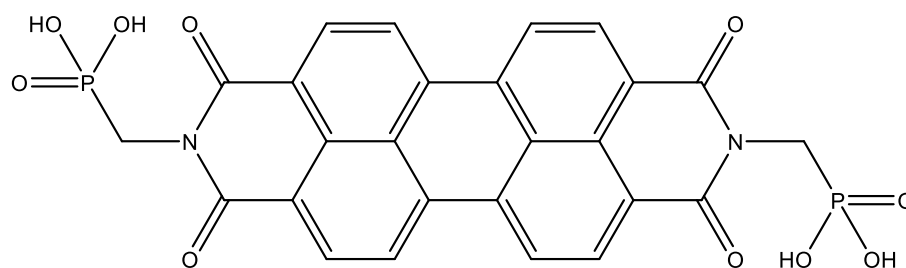


Figure 1.4. Structure of *N,N'*-bis(phosphonomethyl)-3,4,9,10-perylenediimide (PMPDI)

Work prior to this dissertation studied the PMPDI- CoO_x dye-catalyst combination in two systems / architectures. In an initial, 1st generation, device a thick layer of the PMPDI was spin

coated onto conductive glass and CoO_x catalyst was deposited.⁷⁷ This simple device was shown to photoelectrochemically oxidize water with a photocurrent density of $150 \mu\text{A}/\text{cm}^2$ at +1.0 V applied bias versus Ag/AgCl and with a faradaic efficiency of $80 \pm 15\%$ at +900 mV applied potential versus Ag/AgCl.⁷⁷ However, this device is limited by poor light absorption (only 12% of incident light under simulated solar conditions was absorbed at the PMPDI's λ_{max}) and very high charge carrier recombination (6% charge transport efficiency even at the +1.0 V applied overpotential).⁷⁷ As such, this device was modified to a second generation DS-PEC with the addition of a nano- SnO_2 scaffolding to both increase surface area for dye adsorption and decrease the thickness of the PMPDI layer down to a near monolayer to reduce exciton diffusion lengths and, thereby, associated recombination.⁴² Light absorption increased to ca. 100% with this new architecture and charge transport efficiency increased in the device as well.⁴² However, photoelectrochemical deposition of the same known WOCatalyst, CoO_x , results in a *decrease* in photocurrent and an increase in recombination, an unexpected “anti-catalyst” result opposite to the goal of enhanced catalysis upon addition of the known WOCatalyst, CoO_x .⁴² Kirner et al. hypothesized that this decreased photocurrent upon catalyst addition is due to recombination between catalyst deposited directly onto the nano- SnO_2 , Figure 1.5.

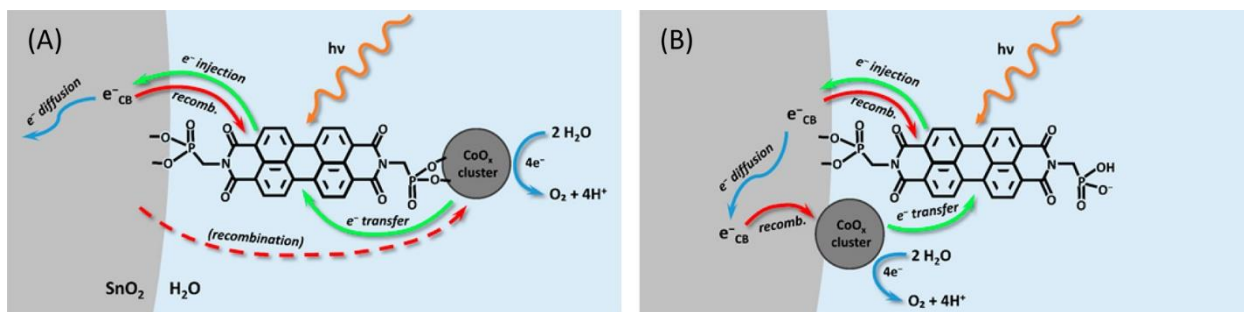


Figure 1.5. (A) Hypothesized idealized binding scheme of PMPDI and CoO_x ; (B) Hypothesized more realistic, data-based binding scheme of PMPDI and CoO_x . Green arrows indicate charge transfer reactions leading to water oxidation while red arrows indicate charge recombination reactions. Figure reproduced with permission from reference 42. Copyright 2017 American Chemical Society.

Understanding the source of this “anti-catalyst” effect and how best to overcome the increased recombination is of great importance not only to improve this system, but also to understand and develop related, improved devices. Hence, the research in this dissertation focuses on developing and implementing different strategies to outcompete recombination in this DS-PEC device resulting in improved photoactivity. Additionally, the research herein seeks to use characterization and controlled experiments designed to identify the source of the recombination in this system.

Chapter II of this dissertation looks to understand the impact of an alumina overlayer on our previously published photoanode.⁴² This chapter was published in the journal *Sustainable Energy Fuels* (Jewell, C. F.; Subramanian, A.; Nam, C-Y; Finke, R. G. *Sustainable Energy Fuels*, **2021**, *5*, 5257-5269. DOI <https://doi.org/10.1039/D1SE00908G>). In this paper, a layer of alumina was added to the nano-SnO₂ after dye deposition, but before catalyst addition, with the goal of understanding the source of the hypothesized CoO_x and the nano-SnO₂ recombination. Five key questions were discussed in this paper, including the question of if the addition of a ca. 1 nm-thick AlO_x layer deposited on a 4000 nm (i.e., 4 micron) thick mesoporous anode system would even begin to alter the water oxidation catalysis properties of the device. Ultimately, the presence of an ultrathin alumina overlayer by atomic layer deposition (ALD) was shown to improve photocurrents by 2.5-fold by reducing charge-carrier recombination with a 0.6 nm-thick AlO_x layer deposited at 85 °C providing the best photocatalytic activity we observed. However, the addition of the CoO_x catalyst still decreases the photocurrent, even in devices with an alumina overlayer. The study also proposes a kinetic scheme for recombination pathways in the device.

Chapter III identifies residual carbon in the nanostructured SnO₂ as a major source of recombination in the same SnO₂/PMPDI/CoO_x water-oxidation system. This chapter was published in the journal *ACS Applied Materials & Interfaces* (Jewell, C. F.; Subramanian, A.;

Nam, C-Y; Finke, R. G. *ACS Appl. Mater. Interfaces*, **2022**. DOI <https://doi.org/10.1021/acsami.2c02692>). This paper strives to understand the source of the “anti-catalyst” effect described above in which the addition of a known WOCatalyst decreases the photocurrent. Residual carbon impurities from organic stabilizers used in the nanostructured SnO₂ synthesis were identified as the source of the “anti-catalyst” effect using a series of control experiments varying the amount of carbon. Additional evidence was provided using ALD deposition, in this case more carbon-free planar SnO₂ was deposited instead of nanostructured SnO₂. With the significantly decreased amount of carbon in the ALD-SnO₂, the addition of the cobalt oxide WOCatalyst yields an *increase* in photocurrent. Additionally, a brief “Perspective and Suggestions for the Field Going Forward” is provided with the goal of highlighting the ubiquitous problem of defects in metal-oxides and carbon impurities and ways to get around these issues.

Chapter IV reports additional studies designed to overcome recombination attributable to residual carbon in the DS-PEC water-oxidation device described above. That chapter is being prepared for submission in the Summer of 2022. Two methods to overcome or avoid the residual carbon problem discussed in Chapter III are presented: first, the use of an iridium-based catalyst, amorphous Li-IrO_x, is used instead of CoO_x to test the hypothesis that using a more catalytically active (i.e., “better”, more efficient at charge collection and transfer) catalyst can overcome and outcompete recombination, generating an increase in photocurrent. Improving the WOCatalyst to Li-IrO_x is shown to change the charge transfer kinetics such that the WOCatalyst can, indeed, overcome and outcompete recombination pathways. In a second approach to the recombination issue, planar, more carbon-free ALD-SnO₂ anodes are tested for their performance versus their nanostructured counterparts. Specifically, ALD-SnO₂ anodes were shown to outperform

nanostructures SnO₂ anodes, in both cases coated with PMPDI and using CoO_x as a WOCatalyst, post correcting for either the electrochemically active surface area or the dye adsorption.

The final chapter of this dissertation, Chapter V, summarizes the key results from the research described in this dissertation. The results and conclusions from each study are combined with literature knowledge to predict the most impactful future directions for the project and field as a whole.

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II. ULTRATHIN ALUMINA PASSIVATION FOR IMPROVED PHOTOELECTROCHEMICAL WATER OXIDATION CATALYSIS OF TIN OXIDE SENSITIZED BY A PHOSPHONATE-FUNCTIONALIZED PERYLENE DIIMIDE FIRST WITHOUT, AND THEN WITH, COBALT OXIDE¹

OVERVIEW

Previously, a photoanode composed of nanostructured SnO₂ coated with the perylene diimide dye N,N'-bis(phosphonomethyl)-3,4,9,10-perylenediimide (PMPDI) plus photoelectrochemically deposited cobalt oxide (CoO_y) was shown to photoelectrochemically oxidize water at $31 \pm 7\%$ Faradaic efficiency. A non-ideal part of that prior system is that the addition of the known CoO_y water oxidation catalyst (WOC) resulted in a *reduction* of the total photocurrent rather than the anticipated increase, due to an increase in charge-carrier recombination. Herein, we show deposition of an ultrathin alumina overlayer applied by atomic layer deposition (ALD) on the SnO₂/PMPDI photoanode can improve the photoactivity and catalytic activity of the system; the addition a ca. 1-nm-thick AlO_x layer deposited on a 4000 nm (*i.e.*, 4 micron) *thick mesoporous* anode system can and does have a positive, 2.5-fold improvement in the steady-state photocurrent with $29 \pm 9\%$ Faradaic efficiency vs the control anode without alumina

¹ This chapter details the preparation, characterization, and photoelectrochemical study of the impact of the addition of an alumina overlayer on a dye-sensitized photoelectrochemical system for water oxidation catalysis. This chapter was published in the journal Sustainable Energy and Fuels (Jewell, C. F.; Subramanian, A.; Nam, C.-Y.; Finke, R. G. *Sustain. Energy Fuels* **2021**, 5, 5257–5269. <https://doi.org/10.1039/d1se00908g>), and which has been reproduced with permission. The article is licensed under the Royal Society of Chemistry, and further permission requests related to the article should be directed to the RSC. The project described in this chapter was conceived by the PI, Prof. Finke. The author of this dissertation, C. F. Jewell, conducted *all* experiments and data analysis with the exception of the atomic layer deposition procedure. Minor changes to the manuscript have been made to meet dissertation formatting requirements. The supporting information can be found in Appendix I.

passivation by reducing charge-carrier recombination. Moreover, ALD-deposited AlO_x layer does help support the understanding of the “anti-catalysis” of co-depositing a CoO_y WOC on the SnO_2 /PMPDI DS-PECs—specifically the picture of direct CoO_y - SnO_2 contact-mediated recombination—but that AlO_x layer was unable to improve the photocurrent in a net SnO_2 /PMPDI/ AlO_x /(CoO_y) system. We attribute the lack of a performance enhancement by CoO_y WOC to incomplete coverage of each SnO_2 nanoparticle by the AlO_x . Overall, we find the addition of an optimized *ultrathin* AlO_x layer (0.6 nm thick; deposited at 85 °C) improves the SnO_2 /PMPDI/ AlO_x system’s photoactivity by a factor of up to ca. 3-fold with reduced recombination. These results document that metal-oxide passivation by low-temperature ALD can be an effective strategy for improving the water oxidation performance of even nanostructured dye sensitized-photoelectrochemical cells.

INTRODUCTION

Efficient photoelectrochemical solar water splitting into molecular hydrogen and oxygen is one of the must-solve problems in chemistry^{1,2} en route to fulfilling the growing global demand for clean, renewable energy while minimizing CO_2 emissions.^{3–7} Recently, the application of *organic* dyes as light absorber for solar water splitting has drawn extensive attention due to their relatively low cost, their production from earth-abundant materials, the ease of processability, and the ability to synthetically tailor the organic dye as needed to optimized water-splitting performance.^{4,8} Previously, we developed a first,⁹ then a second¹⁰ generation water-oxidation photoanode using both organic thin-film and dye-sensitized photoelectrolysis cell (OTF-PEC and DS-PEC) architectures based on a perylene diimide dye derivative ($\text{N,N}'$ -bis(phosphonomethyl)-3,4,9,10-perylenediimide, PMPDI, Figure 2.1) and a co-deposited CoO_y water oxidation catalyst (WOC).^{11–}

¹³ Perylene diimides (PDIs) have high light-absorption extinction coefficients (ca. 22,000 M⁻¹ cm⁻¹ at λ_{max} of 500 nm for PMPDI¹⁰) and are used in industrial settings as both car paints and in plastics.⁸ PDIs are further attractive as the light-gathering component in water-oxidation catalysis (WOCatalysis) devices due to their high thermal stability¹⁴, high oxidative stability both in air and in water, and due to their resistance to photobleaching under even extreme conditions, including hypochlorite solutions.¹⁵

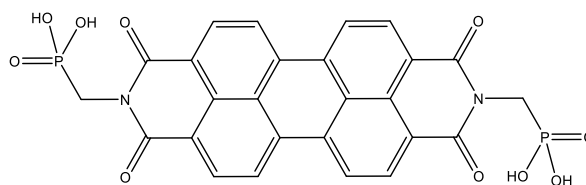


Figure 2.1. Molecular structure of PMPDI

As for the WOC component, CoO_y is an earth-abundant, heterogeneous, prototype WOC.¹⁶ Our previous study on the PMPDI OTF-PEC architecture showed a 10-fold enhancement of water-oxidation photocurrent by applying co-deposited CoO_y as the WOC⁹, but the system exhibits a low light-harvesting efficiency (LHE) (ca. 12% at λ_{max}) and a large amount of charge carrier recombination, yielding only a 6% charge transport efficiency.⁹ An optimized second-generation PMPDI DS-PEC system architecture consisting of nanostructured SnO₂ coated with PMPDI is able to achieve a LHE of >99% at λ_{max} and a charge transport efficiency of 13%.¹⁰ However, it was found that the same CoO_y WOC, necessary to produce oxygen, in fact *decreased* the water oxidation performance in the second-generation SnO₂/PMPDI/CoO_y system relative to the first.^{9,10} That unexpected, undesired, “anti-catalyst” behavior was attributed to increased charge recombination between photoinjected electrons in the SnO₂ conduction band and accumulated holes in CoO_y at the SnO₂ surface.^{10,17,18} More generally, that “anti-catalyst” behavior illustrates

the acknowledged broader challenge¹⁹ of coupling water-oxidation as well as other catalysts to light-absorbing units in ways that minimize charge-carrier recombination back reactions.

To begin to address the forefront question of how to best couple catalysts and light-absorbing units, we previously attempted to improve the performance of SnO₂/PMPDI/CoO_y DS-PECs by using a wet chemical method¹⁰ to deposit a thin layer of electronic insulator AlO_x on the SnO₂ surface as an established tunneling barrier^{17,20} against recombination. That effort led to an improved photovoltage, but a reduced photocurrent due to a hindered charge injection between the dye and SnO₂.¹⁰

In related work, Kamire and coworkers reported reduced charge recombination by applying 0.5 – 3 nm thick ultrathin AlO_x coating directly over dyes by atomic layer deposition (ALD) in a DS-PEC system consisting of nano-TiO₂ sensitized by a perylene monoimide (PMI) dye.²¹ The observed decreased recombination was attributed to the passivation of recombination-active TiO₂ surface states and to an increased barrier for tunneling-based recombination with redox-active species in solution.²¹ The addition of the AlO_x layer further served to stabilize the dye, resulting in improved device lifetimes. Significantly, Kamire et al. observed that the addition of an Ir-dimer-based WOC resulted in a ca. 66% *reduction* of photocurrent, both with and without the AlO_x overlayer²¹, closely analogous to what we have observed in our previous study where the addition of the known WOC¹⁶ CoO_y decreased the photocurrent output of the SnO₂/PMPDI DS-PEC.¹⁰ These examples make apparent the forefront problem of effectively coupling the DS-PEC systems to desired catalysts, such as a WOC, without, instead, enhancing undesirable recombination. These studies further suggest the hypothesis that the performance of DS-PECs and catalysts may be improved if the recombination passivation layer can be further optimized to also allow the WOC to function as desired.

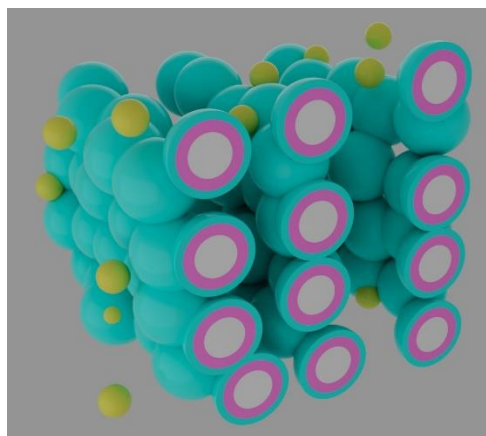


Figure 2.2. Idealized structural models of the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x/\text{CoO}_y$ anode where SnO_2 is grey, PMPDI is pink, AlO_x is blue, and CoO_y is yellow. Nanostructured SnO_2 is reflective of SEM images that will be presented in a figure later in the paper.¹⁰ Anode notation throughout is written in order of deposition, left to right (i.e., SnO_2 is deposited first, followed by PMPDI, then AlO_x , and then finally CoO_y).

Herein, we explore the impact of adding an insulating AlO_x layer prepared by ALD onto a PMPDI-sensitized nanostructured SnO_2 DS-PECs on their solar water splitting performance, idealized by Figure 2.2. More specifically, we address five primary questions via the ALD approach: (i) can the deposition of an ultrathin alumina overlayer applied by ALD on the PMPDI/ SnO_2 photoanode improve the photoactivity and catalytic activity of the CoO_y WOC? More specifically, (ii) can the addition of a 0.6 to 1.3 nm thickness AlO_x layer have any measurable, much less useful effect, on a *4000 nm (i.e., 4 micron) thick and also nanoporous* anode system? If so, (iii) what are the effects of key parameters on the photo- and catalytic-activity, notably the layer thickness and deposition temperature of the alumina overlayer? (iv) Can a better, ALD-controlled deposition of an ultrathin AlO_x layer address the carrier recombination issues of $\text{SnO}_2/\text{PMPDI}$ DS-PECs, and (v) can the ultrathin, ALD-deposited AlO_x layer probe, and perhaps even improve our understanding of why co-deposited CoO_y WOC on the $\text{SnO}_2/\text{PMPDI}$ DS-PECs has, to date, resulted in a decreased, “anti-catalysis” photocurrent? In the present study we investigate the effects of ultrathin AlO_x thickness (0.6 – 1.3 nm) and ALD temperature applied to

a 4 μm thick DS-PEC photoanode system on the overall anode photoactivity, device/organic dye stability, and, importantly, on the catalytic activity of the CoO_y WOC by characterizing the system's open-circuit photovoltage, photocurrent, and O_2 product yield and hence Faradaic efficiency under solar PEC water splitting conditions. The results allow insights into the five questions posed that form the basis for the present research. In addition, the studies which follow make apparent when and how ALD-deposited alumina layers should or should not be used to try to improve analogous DS-PECs, the needed considerations of layer thickness, and factors to be considered when using ALD on nanostructured devices. The results provide a working hypothesis for going forward about how to couple WOC and other catalysts to DS-PECs for improved catalyst efficiency.

EXPERIMENTAL

Materials. The following starting materials and solvents were used as received to generate buffer solutions: KOH (Fisher, Certified ACS grade, 98.5%, 1.5% water, 0.00028% Fe, 0.0008% Ni); KH_2PO_4 (Fisher, Certified ACS Grade, 99.3%, 0.0005% Fe); hydroquinone (Aldrich, >99%); NANOpure water (Barnstead NANOpure ultrapure water system, 18.0 M Ω). NANOpure water was used for all experiments.

Synthesis of PMPDI dye, and the deposition of SnO_2 anode and CoO_y WOC. All synthetic and manufacturing details for PMPDI dye and the SnO_2 anodes can be found in our previous publications^{9,10}. Briefly, the anodes are composed of fluorine-doped tin oxide (FTO)-coated glass as a transparent current collector, covered by a mesoporous SnO_2 film, sensitized with PMPDI, and CoO_y WOC. All fabricated photoanodes have SnO_2 film with “2-Scotch” layer thickness conditions¹⁰ where PMPDI dyes were loaded for 24 hr at 95 °C from a saturated solution of fully

protonated PMPDI in water.¹⁰ CoO_y WOC was added to photoanodes by photoelectrochemical deposition^{9,10}; the anodes (SnO₂/PMPDI or SnO₂/PMPDI/AlO_x) were submerged in a solution of pH 7, 0.5 mM Co(NO₃)₂ and 0.1 M potassium phosphate buffer (KPi) and held at +0.2 V vs Ag/AgCl under 1 sun illumination for 3 min.¹⁰ Anodes were then rinsed with water for 30 s and allowed to air dry.

Ultrathin AlO_x coating by ALD. Ultrathin conformal AlO_x layer was deposited on PMPDI or glass substrate using a Cambridge Nanotech Savannah S100 ALD system (base pressure ~ 0.4 Torr). The deposition temperature was set at 85 °C; PMPDI was shown to be stable up to 400 °C herein. The depositions were carried out by sequential exposure of trimethyl aluminum (TMA) (14 ms) and water vapor (40 ms) with an intermediate purge time of 60 s for both precursors. Spectroscopic ellipsometry was used to calibrate the AlO_x thickness per ALD cycle using Si control substrates and found a linear growth rate of 0.067 nm per cycle (Figure S2.1 and Table S2.1; see Appendix I for details). The number of ALD cycles was varied between 4 and 28 to deposit AlO_x on SnO₂/PMPDI or glass substrates ranging between 0.4 and 2.0 nm, respectively. In a separate set of experiments, the ALD temperature has been varied from 85, 150, and to 200 °C to investigate the impact of deposition temperature on the device performance. AlO_x deposition was verified using scanning electron microscopy (SEM) imaging and X-ray photoelectron spectroscopy (XPS) methods, *vide infra*.

Photoelectrochemical testing. All photoelectrochemical experiments were done in a previously described¹⁰ custom two-compartment Pyrex cell consisting of a working compartment (1 × 1.5 × 1.5 cm³, 5 ml) and an auxiliary compartment separated by a medium porosity glass frit. Experiments were conducted using a CH Instruments CHI630D potentiostat, a Pt wire counter electrode positioned in the auxiliary compartment and a Ag/AgCl (3 M NaCl, +0.215 V vs normal

hydrogen electrode (NHE)) reference electrode positioned in the working compartment in close proximity to the anode surface. The anode was clamped with an alligator clip to the front wall of the working compartment with the uncoated, nonconductive glass side pressed against the cell wall. The cell was filled with ca. 5 ml electrolyte (pH 7, 0.1 M KPi buffer) sufficient to cover the film. The anode was illuminated from the substrate side using a 65 W xenon arc lamp (PTO model A1010), which was powered by an OLIS XL150 adjustable power supply. The light passed through a bandpass filter (315 – 710 nm, Thorlabs KG3, FGS900S) and an ultraviolet (UV) filter (400 nm long-pass, Thorlabs FGL400S). The power density of the light was adjusted to reflect the visible region of the airmass 1.5 global (AM 1.5G) spectrum.¹⁰ In the experiments in which transients (interrupted illumination) of 5 s or 30 s were used, a manual shutter was used to block the light.¹⁰ Each anode was tested with a series of electrochemical experiments in the order detailed below. First the cell was allowed to short-circuit in the dark for 60 s to depopulate the electrons from SnO₂ sub-bandgap states.¹⁰ The 60 s was determined to be a sufficient length of time to depopulate the excited state as the current reached a steady-state within 15 s. Then the open-circuit potential, V_{oc} , was measured vs the Ag/AgCl reference electrode for 90 s in the dark and then measured again under illumination for 90 s. Next, a photocurrent transient experiment was performed in which the anode was held at +0.2 V vs Ag/AgCl for 300 s with 30 s light/dark transients throughout. A potential of +0.2 V vs Ag/AgCl was chosen for photocurrent transient experiments as photocurrent is fully saturated by this applied potential. The cell was again allowed to short-circuit in the dark for 60 s, and the V_{oc} in both the dark and light were remeasured. Then the current-voltage (i - V) photocurrent transient experiment was performed. The voltage was scanned from -0.2 to +1.0 V vs Ag/AgCl with a 10 mV/s scan rate and 5 s light transients. Each experiment was reproduced a minimum of three times with three separate anodes produced under

identical conditions. All figures and values reported herein are representative of the photoactivity of the system indicated. Care was taken to ensure that the reported results are reproducible and not due to a defective anode or otherwise irreproducible sample.

IPCE and APCE Determinations. Incident photon to current efficiency (IPCE) measurements were calculated from action spectra collected using a Xe arc lamp (Oriel model 66002, calibrated to approximate the AM1.5 reference power in the visible region), power supply (Oriel model 68700), monochromator (Oriel Cornerstone 130, model 7400), and a CH Instruments 630D potentiostat. All experiments were run in the presence of 20 mM H₂Q sacrificial agent in pH 7 0.1 M KPi buffer using the same two-compartment Pyrex cell used for all photoelectrochemical testing; a Pt wire counter electrode positioned in the auxiliary compartment and a Ag/AgCl (3 M NaCl, +0.215 V vs normal hydrogen electrode (NHE)) reference electrode positioned in the working compartment in close proximity to the anode surface were again used. In order to collect the action spectra, the electrode being test was held at +0.2 V vs Ag/AgCl while incident monochromatic light (ca. 3 nm bandwidth) was scanned from 400 to 700 nm across 25 nm intervals. A silicon standard power sensor (Thorlabs model S120B) was used to measure the incident lamp power through the same aperture at each wavelength, P_{mono} . Photocurrent, I_{ph} , was measured at each wavelength by recording the photocurrent during three 15 second light transients and subtracting off any dark current. The average photocurrent was then used to calculate the IPCE according to equation 2.1:

$$IPCE(\lambda) = \frac{I_{ph}(mA) \times 1239.8 (V \cdot nm)}{P_{mono}(mW) \times \lambda(nm)} \quad \text{eq. 2.1}$$

The absorbed-photon-to-current efficiency (APCE) was calculated by dividing the light harvesting efficiency (LHE)—i.e., the absorptance spectrum measured from the anode—out of

the IPCE, using equation 2.2. Note that the APCE is equivalent to the injection efficiency, ϕ_{inj} , multiplied by the charge collection efficiency, η_{col} .

$$APCE = \frac{IPCE}{LHE} = \phi_{inj} \eta_{col} \quad \text{eq. 2.2}$$

Oxygen detection. Oxygen yield was experimentally measured using the generator–collector (G-C) technique detailed elsewhere:^{10,22–24} photoanode ‘generators’ were sandwiched with an FTO ‘collector’,¹⁰ separated by a Parafilm spacer. A CH Instruments CHI-750D bipotentiostat was used for the G-C experiments. The G-C cell was placed in the previously detailed working compartment with the generator side against the wall of the cell with the incoming light. The cell was filled with pH 7, 0.1 M KPi buffer, approximately 10 ml, which was degassed with Ar for a minimum of 30 min. An Ag/AgCl (3 M NaCl) electrode was used as a reference and was also placed in the working compartment. A Pt wire was used as a counter electrode and was placed in the auxiliary compartment. Current was measured at both the generator and collector electrodes, which were held at +0.2 V and –0.65 V vs Ag/AgCl, respectively. The current was collected for 300 s in the dark, 300 s in the light, then 300 s in the dark in order to ensure that all oxygen had diffused across the two electrodes and that all current attributable to oxygen production was collected. Control experiments with FTO/CoO_y anodes were used to determine the collection efficiency of the sandwich configuration and used to calculate the O₂ yield and Faradaic efficiency of each photoanode.

RESULTS AND DISCUSSION

The effects of AlO_x overlayer on the photoelectrochemical activity of SnO₂/PMPDI

As noted in the Introduction, the addition of an electronically insulating metal-oxide shell layer over the mesoporous semiconductor substrate (and sometimes the dye as well) has been

shown to reduce recombination and increase photocurrents in dye-sensitized systems.^{17,20,21,25–32}

In a previous study, 1.3 nm thick metal oxide deposited at 85 °C was found to be optimal for a photoanode system based on organic semiconductor thin films.²⁸ Hence, as to start and as a baseline, a 1.3 nm thick layer of AlO_x was deposited at 85 °C by ALD onto the previously optimized¹⁰ PMPDI-sensitized mesoporous SnO_2 .

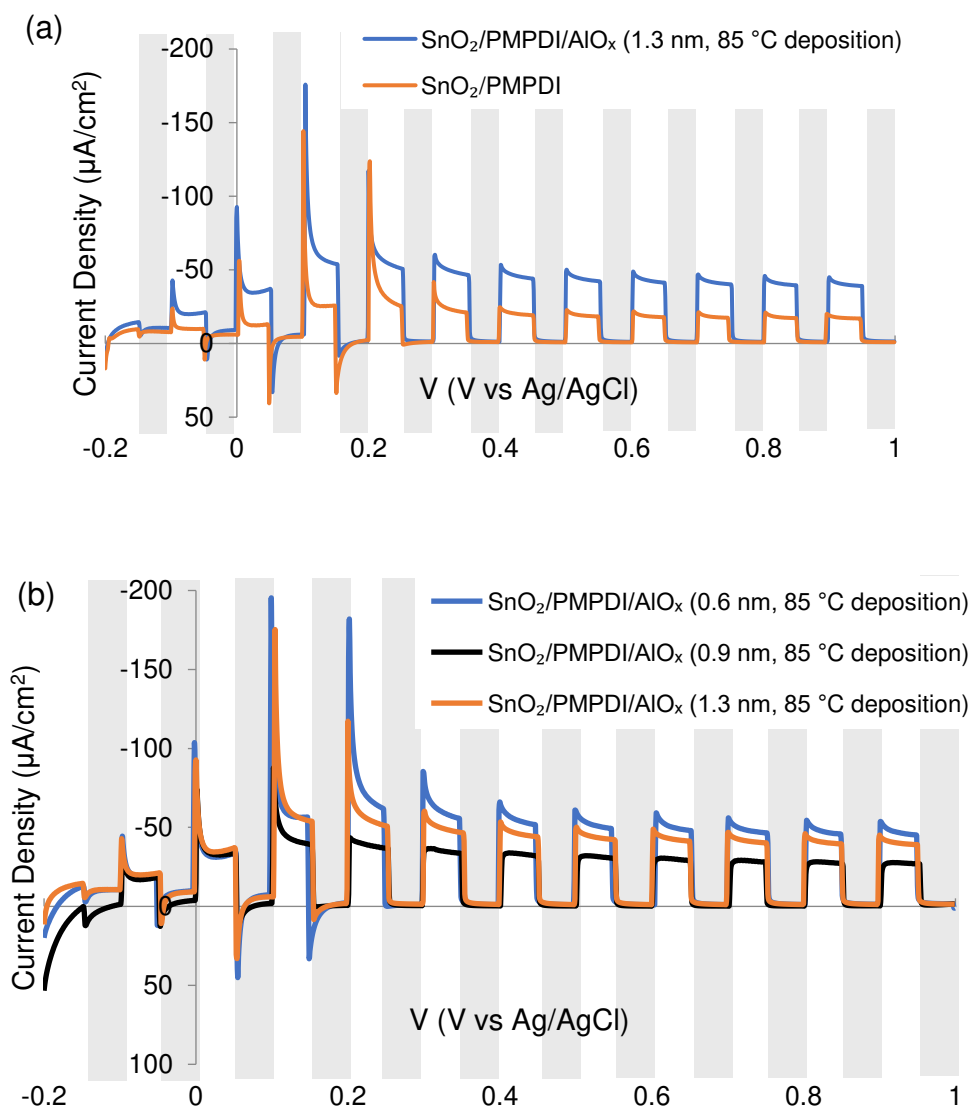


Figure 2.3. Photocurrent transients (indicated by light (light-on)/ dark (light-off) shading, 5 s each) collected in pH 7, 0.1 M KPi electrolyte for: (a) $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (1.3 nm, 85 °C deposition temperature, blue) and $\text{SnO}_2/\text{PMPDI}$ (red) anodes.; (b) $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (0.6 nm, 85 °C deposition, blue), $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (0.9 nm, 85 °C deposition, black) and $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$

(1.3 nm, 85 °C deposition, red) anodes. Comparatively thinner, 0.6 nm, layers of alumina yield higher photocurrents than their 0.9 and 1.3 nm counterparts.

Photoactivity was recorded for each anode tested in a scanning voltammetry experiment coupled with light/dark phototransients (Figure 2.3a). Working from left to right, the voltage is scanned from -0.2 to $+1.0$ V vs Ag/AgCl with a 10 mV/s scan rate. For each of the phototransients, illumination of the photoanode causes a rapid rise in anodic (negative y-axis) current and then blocking of the light each 5 s causes the rapid drop in current. The large current spikes observed at ca. $+0.1$ V vs Ag/AgCl are also present on bare SnO₂ anodes,¹⁰ indicating that the spikes cannot fully be attributed to PMPDI, but are likely related to SnO₂ recombination centers.^{10,17}

We find that by the addition of the 1.3 nm of AlO_x overlayer deposited at 85 °C, SnO₂/PMPDI/AlO_x, significantly increased both peak and steady-state photocurrent by approximately 1.6-fold and 2.5-fold, respectively, compared with the system without any AlO_x (Figure 2.3a). The increased peak and steady-state photocurrents suggest that the charge carrier production/collection is increased, likely due to a reduced carrier recombination. Note, the deposition of AlO_x has negligible effect on the absorbance spectrum of the SnO₂/PMPDI electrode (Figure S2.2) and alumina itself was shown not to produce significant photocurrent on its own, indicating that AlO_x is likely not functioning as a major WOC (Figure S2.3). The addition of AlO_x also reduces the ratio of peak to steady-state anodic photocurrent (i.e., current ‘spiking’ behavior), which is often attributed to charge recombination caused by metal-oxide surface states.^{10,17,33–35} The SnO₂/PMPDI system displayed ca. 87% anodic decay from peak to steady-state photocurrent over 5 min at $+0.2$ V vs Ag/AgCl, while the SnO₂/PMPDI/AlO_x decayed slightly less, ca. 76%. This spiking behavior can also be indicative of photocorrosion due to excessive charging of the light absorber.³⁶ Photocorrosion is certainly an issue in tough oxidative reactions, such as water splitting, and as such these same experiments were carried out using hydroquinone (H₂Q) (Figure

2.4). With the addition of hydroquinone, the spiking behavior is minimized, suggesting that the more kinetically and thermodynamically facile reaction can outrun the recombination pathways. In short, increasing the desirable kinetic pathways with the addition of H_2Q can overcome the recombination pathways. Overall, these observations are consistent with the partial passivation of surface trap states on SnO_2 and PMPDI by 1.3 nm thick AlO_x .

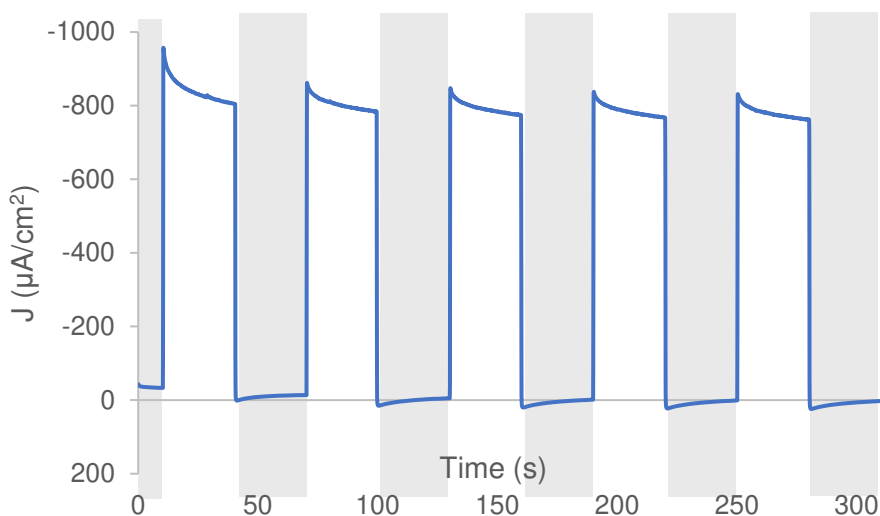


Figure 2.4. Photocurrent transients (with 30 s light/dark intervals) for a representative $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x/\text{CoO}_y$ (0.6 nm, 85 °C deposition) anode. Transients were performed at +0.2 V vs Ag/AgCl in pH 7, 0.1 M KPi buffer with 20 mM H_2Q . Background H_2Q currents were subtracted off.

To maximize the device performance enhancement by the AlO_x anode passivation layer, it is necessary to optimize the thickness of AlO_x that balances its benefits (e.g., surface state passivation and reduced carrier recombination) with the possible decrease in photoactivity from an ineffective charge transfer between the semiconductor to electrolyte, a decreased surface area, or separation of the dye from the catalyst, all of which can be caused by a too thick AlO_x overlayer. Alumina is an insulator and hence functions as a tunneling barrier. Finding a balance between moving charge carriers through the AlO_x and fully covering the SnO_2 is fundamentally important to minimizing recombination while maintaining charge carrier movement, that is, optimizing the kinetics.

However, there is largely inconsistent information in the literature as to the optimal thickness of ALD overlayer in DS-PEC systems, with reports ranging from sub-monolayer to 3 nm.^{21,25,28,37–42} Therefore, a series of anodes with varying overlayer thicknesses from 0.6 nm to 1.3 nm were investigated (Figure 2.3b) in order to determine the thickness at which the kinetics are optimized, which will be discussed herein and is detailed below in Figure 2.9. We find that the photocurrent was maximized with relatively thinner AlO_x layer, reaching, for example, $-182 \mu\text{A}/\text{cm}^2$ at +0.2 V vs Ag/AgCl for 0.6 nm AlO_x, compared with -64 and $-115 \mu\text{A}/\text{cm}^2$ for 0.9 nm and 1.3 nm thick AlO_x, respectively. This result illustrates that an even modestly thicker AlO_x passivation layer can indeed interfere with the charge transfer between the anode and electrolyte, consistent with previous literature.⁴³

As illustrated in Figure 2.3, we find that the photocurrent spiking behavior still exists regardless of the AlO_x passivation thickness. Considering that photocurrent spiking is often attributed to metal oxide surface trap states,^{10,33,35,44} we tested if increasing the AlO_x deposition temperature could affect the spiking behavior, since higher AlO_x ALD temperature should in principle result in the growth of more stoichiometric Al₂O₃ with reduced defect density and increased coating uniformity.^{45–50,51} X-ray photoelectron spectroscopy (XPS) was done in an attempt to detect distinct environments between the alumina depositions, but no differences were observed (Figure S2.4). Specifically, SnO₂/PMPDI anodes were coated with 0.6 nm of AlO_x at 85 °C, 150 °C, and 200 °C, and their photoelectrochemical activities were compared (Figure 2.5). Interestingly, the increased AlO_x ALD temperature resulted in a rather minor increase in the extent of photocurrent spiking, while *decreasing* the overall photocurrent. To quantify the photocurrent spiking behavior, we calculate the percentage of photocurrent decay from peak to steady state measured at +0.2 V vs Ag/AgCl from each system. The SnO₂/PMPDI/AlO_x systems with AlO_x

deposited at 85, 150, and 200 °C displayed a photocurrent decay of ca. 76%, 84%, and 83%, respectively. In the meantime, the photocurrent peak decreased from $-182 \mu\text{A}/\text{cm}^2$ at $+0.2 \text{ V}$ vs Ag/AgCl for the AlO_x deposited at 85 °C to -107 and $-92 \mu\text{A}/\text{cm}^2$ for the AlO_x deposited at 150 and 200 °C, respectively. However, regardless of deposition temperature, the addition of AlO_x overlayer still yielded a higher photocurrent than the neat PMPDI, consistent with the role of AlO_x mitigating as desired against charge carrier recombination.

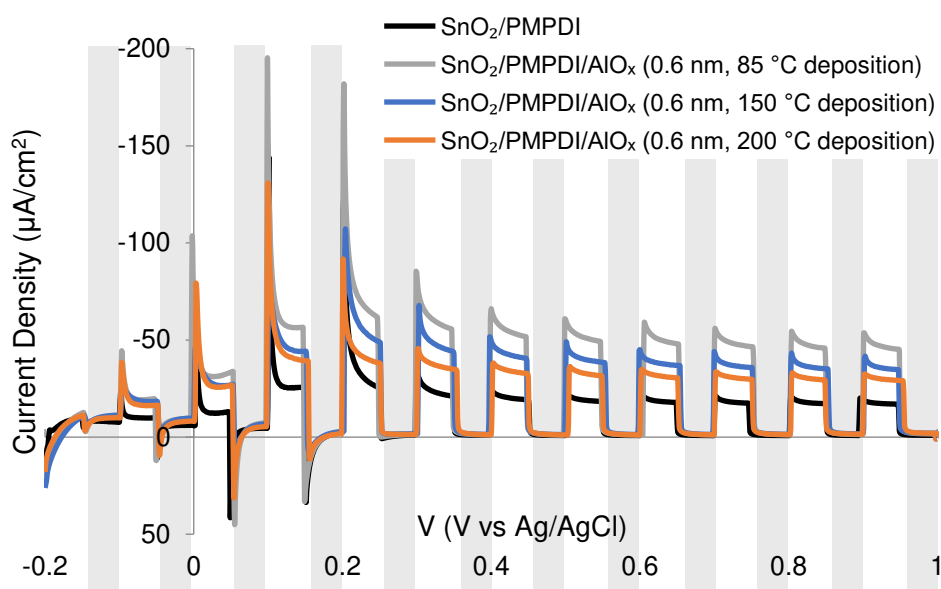


Figure 2.5. Photocurrent transients (indicated by light (light-on)/ dark (light-off) shading, 5 s each) collected in pH 7, 0.1 M KPi electrolyte for $\text{SnO}_2/\text{PMPDI}$ (black), $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$, (0.6 nm, 85 °C deposition, green), $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$, (0.6 nm, 150 °C deposition, light blue), and $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$, (0.6 nm, 200 °C deposition, red) anodes. Scans were run from -0.2 to $+1.0 \text{ V}$ vs Ag/AgCl. Increasing the deposition temperature of AlO_x yielded a decrease in photocurrent.

A control experiment was performed to show that the decrease in photocurrent at higher AlO_x ALD temperature is not caused by the thermal degradation of PMPDI during ALD. Specifically, thermogravimetric analysis (TGA) confirmed the stability of PMPDI up to 400 °C (Figure S2.5), consistent with the generally reported thermal stability of PDI to approximately 300–600 °C,¹⁴ so that the ≤ 200 °C used herein should not be a problem unless there was efficient catalysis of PMPDI

decomposition by the deposited AlO_x . This latter possibility was ruled out by a second control experiment demonstrating the unchanged optical absorption spectrum of a photoanode before and after the ALD at the elevated, up to 200 °C temperatures employed (Figure S2.2). The interesting higher photocurrent observed from the AlO_x layer deposited at the *lower* temperature might be associated with the surface states at AlO_x being able to serve as mediators for the photocatalytic reaction, increasing the overall photocatalytic activity of PMPDI^{28,52}, an intriguing working hypothesis for going forward and possible further investigation.

In all cases with added catalyst, the photocurrents observed in the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ systems are not attributable to water oxidation, consistent with findings in the original $\text{SnO}_2/\text{PMPDI}$ system.¹⁰ We hypothesize that perhaps the photocurrent could be due to some combination of dye degradation (though dye losses are minimal and even full dye degradation cannot account for all charge passed)¹⁰, oxidation of water to H_2O_2 , and oxidation of trace impurities.

Incident-photon-to-current efficiency (IPCE) and Faradaic efficiency of $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ photoanodes

The IPCE of the optimized $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (0.6 nm, 85 °C) was measured to examine the role of AlO_x layer in improving the photocurrent. An action spectrum of the photocurrent vs wavelength of incident light was collected in the presence of the two-electron, kinetically facile sacrificial reductant hydroquinone (H_2Q), $\text{H}_2\text{Q} \rightarrow \text{Q}^{2-} + 2\text{H}^+ + 2\text{e}^-$, Figure 2.6, left.

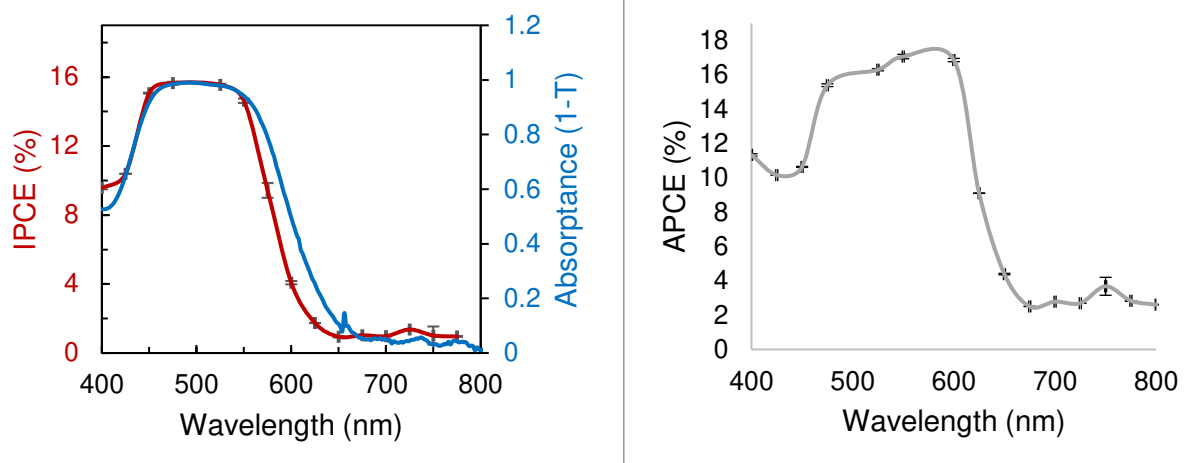


Figure 2.6. (left) IPCE spectrum of SnO₂/PMPDI/AlO_x (0.6 nm, 85 °C deposition) anode in pH 7, 0.1 M KPi buffer with 20 mM H₂Q sacrificial reductant (red) plotted along with the optical absorbance spectrum of PMPDI (blue) and (right) APCE spectra of SnO₂/PMPDI/AlO_x (0.6 nm, 85 °C deposition) anode in pH 7, 0.1 M KPi buffer with 20 mM H₂Q sacrificial reductant.

The IPCE spectrum measured with H₂Q resembles the optical absorbance spectrum of PMPDI dye with some deviation at around 400–450 nm, photocurrent presumably due to some direct absorbance of light by bandgap excitation of SnO₂.¹⁰ By dividing the IPCE by the absorbance of PMPDI, the absorbed photon-to-current efficiency (APCE) was calculated, where the APCE is the internal quantum efficiency of the system, that is the combination of the efficiencies of charge transfer across the semiconductor-electrolyte interface times the charge-collection efficiency at the electrode. The observed APCE is ~18% for the SnO₂/PMPDI/AlO_x (0.6 nm) (Figure 2.6, right), hence modestly superior to those of SnO₂/PMPDI without AlO_x (APCE = ~13%), but ~3-fold superior to the original thin film system, indium doped tin oxide (ITO)/PMPDI with CoO_y WOC (APCE = ~6%)⁹. The observed, higher APCE indicates that more photocurrent is produced for the given number of absorbed photons when the AlO_x overlayer was applied, consistent with the hypothesis discussed: the AlO_x overlayer passivates the defect states at SnO₂ surface thereby reducing charge recombination while the surface states of AlO_x assist the photocatalytic reaction at the electrolyte interface.

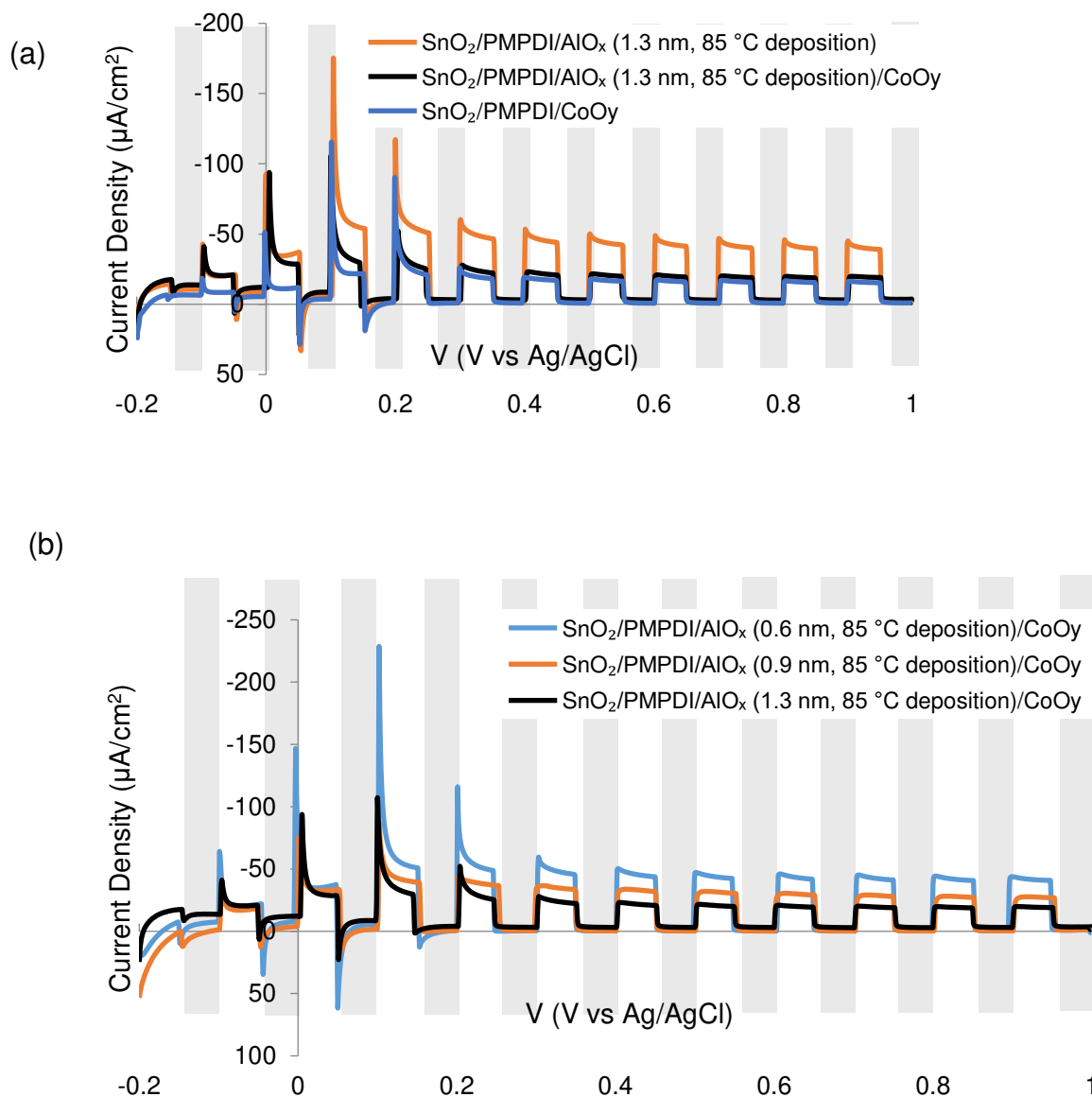
Effects of the combined application of CoO_y WOC and AlO_x passivation layer

We tested if the combination of CoO_y WOC with ALD AlO_x passivation (1.3 nm, 85 °C) could lead to an additional enhancement in water oxidation photocurrent of the SnO₂/PMPDI photoanode. As discussed above, previous reports have shown that the application of WOC to the DS-PEC system with a metal-oxide passivation layer led to an undesired *decrease* in the photocurrent outputs.^{10,21}

We find that the photocurrent in our SnO₂/PMPDI/AlO_x/CoO_y photoanode in fact slightly *increased* over the SnO₂/PMPDI/CoO_y control, indicating that the particular AlO_x passivation layer does not interfere with the catalytic function of CoO_y WOC in our case (Figure 2.7a). Specifically, we observe that the application of AlO_x increases the magnitude of steady-state photocurrent at a given potential for the system (e.g., from $-15\ \mu\text{A}/\text{cm}^2$ to $-19\ \mu\text{A}/\text{cm}^2$ at +0.9 V vs Ag/AgCl for SnO₂/PMPDI/CoO_y and SnO₂/PMPDI/AlO_x/CoO_y, respectively), while decreasing the extent of photocurrent spiking (e.g., at +0.2 V vs Ag/AgCl, 72% decay for SnO₂/PMPDI/AlO_x/CoO_y and 89% decay for SnO₂/PMPDI/CoO_y), consistent with the reduced charge recombination enabled by AlO_x passivation. An extended experiment looking at photocurrent decay in the optimized SnO₂/PMPDI/AlO_x/CoO_y was also carried out, showing approximately 78% decay in photocurrent after ca. 1.5 hours (Figure S2.7).

To the best of our knowledge, this result represents one of the first observations in which the photoanode passivation does not interfere with the activity of CoO_y WOC as compared to the system without the passivation layer deposited onto a PEC. However, the photocurrent from SnO₂/PMPDI/AlO_x/CoO_y photoanodes is still inferior to those of SnO₂/PMPDI/AlO_x counterparts *without* CoO_y WOC (Figure 2.7a), although the origin of the photocurrent from the latter case is still unknown, given that no catalyst or sacrificial reductant were added and no oxygen detected.

Decreasing the AlO_x thickness in the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x/\text{CoO}_y$ photoanode further increases the photocurrent output (Figure 2.7b), similar to the discussed trend in $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ without CoO_y WOC. The sample with the thinnest, 0.6 nm, AlO_x coating achieved the most photocurrent of $-42 \mu\text{A}/\text{cm}^2$ at $+0.9 \text{ V}$ vs Ag/AgCl , which is nearly 2.5 times higher than that obtained for $\text{SnO}_2/\text{PMPDI}/\text{CoO}_y$ without any AlO_x overlayer.



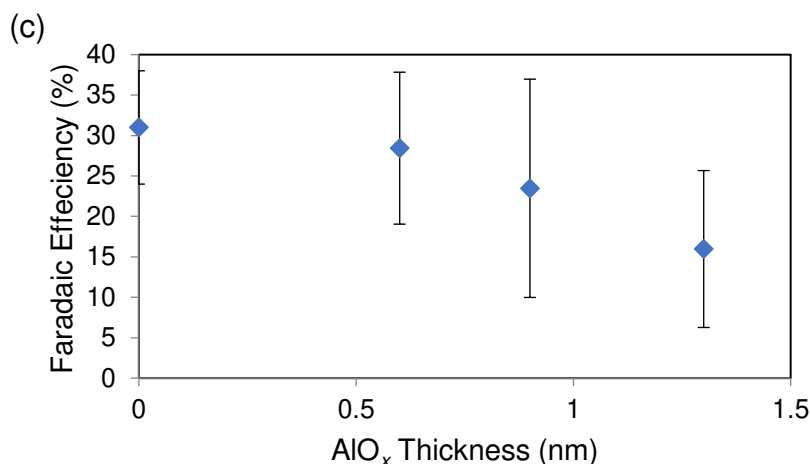


Figure 2.7. Photocurrent transients (indicated by light (light-on)/ dark (light-off) shading, 5 s each) collected in pH 7, 0.1 M KPi electrolyte for: (a) SnO₂/PMPDI/CoO_y (blue), SnO₂/PMPDI/AlO_x (1.3 nm, 85 °C deposition, red) and SnO₂/PMPDI/AlO_x/CoO_y (1.3 nm, 85 °C deposition, black) anodes; (b) SnO₂/PMPDI/AlO_x/CoO_y (0.6 nm, 85 °C deposition, blue), SnO₂/PMPDI/AlO_x/CoO_y (0.9 nm, 85 °C deposition, red), and SnO₂/PMPDI/AlO_x/CoO_y (1.3 nm, 85 °C deposition, black) anodes; (c) Faradaic efficiency values for O₂ generation for SnO₂/PMPDI/AlO_x/CoO_y (85 °C AlO_x ALD) with varying AlO_x thicknesses. In all cases oxygen was produced and the Faradaic efficiency was found to be comparable within error.

We further demonstrate the observed photocurrent is actually derived from water oxidation by measuring Faradic efficiency via the generator–collector (G-C) method^{10,22–24,53} to detect quantitatively the amount of oxygen produced. We find that for all alumina passivation layer thicknesses, the Faradaic efficiency values were largely comparable (Figure 2.7c), with the photoanode passivated by 0.6 nm thick alumina displaying a Faradaic efficiency of $29 \pm 9\%$. This value is within error of that measured from SnO₂/PMPDI/CoO_y without any AlO_x, and samples with thicker AlO_x showed slightly lower average Faradaic efficiencies, though also within error. All samples without catalyst displayed a Faradaic efficiency of 0% prior to CoO_y deposition. Of note, photocurrent decays in extended O₂ generation experiments, 20 minutes, resulted in ca. 11% decay in O₂ generation (S2.8).

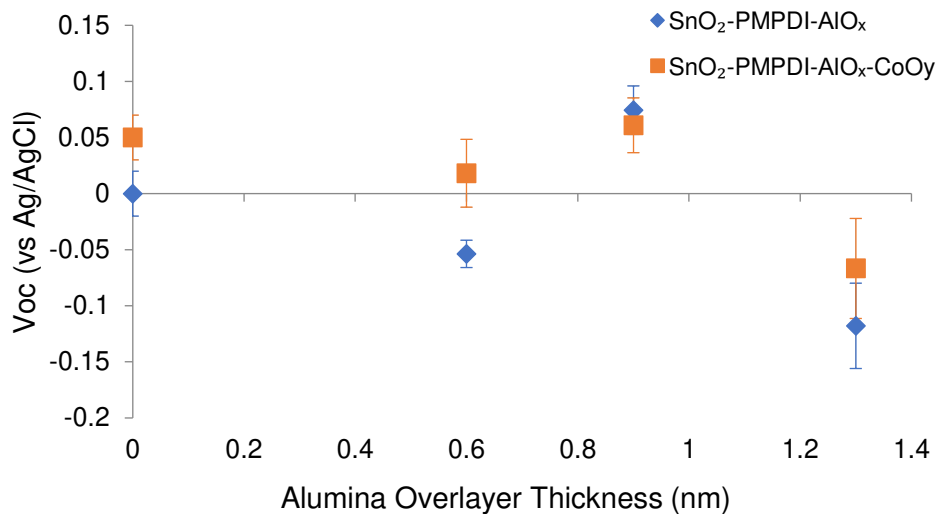


Figure 2.8. V_{oc} vs Ag/AgCl reference electrode in a half-cell setup for SnO₂/PMPDI/AlO_x (85 °C deposition, blue) and SnO₂/PMPDI/AlO_x (85 °C deposition)/CoO_y (red) anodes at differing AlO_x deposition thicknesses. In this case, $V_{oc} \approx E_{F,n}$, the quasi-Fermi energy of electrons in the SnO₂ sub-bandgap states.

We examined the effects of CoO_y WOC on the V_{oc} of SnO₂/PMPDI/AlO_x photoanode with varying AlO_x thickness to understand the impact of CoO_y WOC and AlO_x on the charge recombination and injection (Figure 2.8). When the SnO₂/PMPDI/AlO_x photoanode is illuminated under open circuit, the measured V_{oc} reflects the quasi-Fermi energy of electrons ($E_{F,n}$) in the nano-SnO₂ substrate with respect to a reference electrode potential. The V_{oc} is determined by the steady-state charge-carrier concentration—that is, the quasi-equilibrium—set by the balance between the relative rates of the electron injection from the photoexcited dye to SnO₂ vs the depopulation of the SnO₂ states via recombination^{10,54} (see Figure 2.9 described in more detail below).

Since the addition of the CoO_y WOC in principle should not alter the electron injection rate from PMPDI, any shift in V_{oc} can be attributed to a change in the recombination rate for a given thickness of AlO_x passivation layer.^{10,54} Based on the V_{oc} results (Figure 2.8, Table 2.1), we find a general trend that the measured magnitude of V_{oc} increases while being negative (i.e, the electron quasi-Fermi energy increases due to decreasing rates of recombination relative to injection) as

AlO_x thicknesses increases. This result is as expected if AlO_x acts as a tunneling barrier to electrons leaving SnO_2 . Furthermore, we find a general trend that the measured average V_{oc} is more positive (i.e., the electron quasi-Fermi energy is lower due to increasing rates of recombination relative to injection) after depositing the CoO_y WOC. This result suggests that the CoO_y is able to scavenge electrons from the SnO_2 , despite the AlO_x tunneling barrier, which is consistent with the observed photocurrent results, where photocurrents always decreases for a given AlO_x thickness after depositing CoO_y . The samples with 0.9 nm thick AlO_x appear to be outliers from both trends, showing the most positive V_{oc} (most recombination) and negligible effect of CoO_y on V_{oc} within error. The changing kinetics of the system with differing amounts of alumina reflect the complexity of the kinetics herein, both an advantage and disadvantage of adding a component to a system.

Table 2.1. Open circuit voltage vs Ag/AgCl for varying thicknesses of alumina deposition with and without CoO_y catalyst addition. The addition of CoO_y either increases V_{oc} (0 nm and 0.6 nm of AlO_x) or induces a negligible change (0.9 nm and 1.3 nm AlO_x).

Alumina Thickness (nm)	Voc Without CoO_y	Voc With CoO_y
	vs Ag/AgCl	vs Ag/AgCl
0	0 ± 0.02	0.05 ± 0.02
0.6	-0.054 ± 0.01	0.018 ± 0.03
0.9	0.074 ± 0.02	0.061 ± 0.02
1.3	-0.12 ± 0.04	-0.067 ± 0.04

What is not represented in the kinetic scheme but is crucially important to understanding recombination and efficiency in a WOCatalysis system is the changes in the rate constants for each charge transfer pathway that passes through the AlO_x ‘blocking’ layer. In the case of 1.3 nm thick AlO_x , the V_{oc} is lowest (i.e., most negative), indicating a lowered charge recombination, postulated to be due to a larger tunneling barrier between SnO_2 and CoO_y . Given that 1.3 nm thick AlO_x also results in the lowest amount of photocurrent, this suggests that the comparatively thicker AlO_x passivation layer also slows electron transfer from the CoO_y catalyst to regenerate the photo-oxidized PMPDI, or slows electron transfer from photo-excited PMPDI to SnO_2 . The latter effect is less likely, because the AlO_x overlayer was deposited after PMPDI. Hence, while valuable for beginning to understand the present system in better kinetic detail, future studies testing the pathways in Figure 2.9 and measuring rate constants will be needed to better understand in detail how and why the addition of the AlO_x layer improves photocurrent in the present system.

Structural model for AlO_x passivation layer and CoO_y WOC

A typical assumption in the dye-sensitized solar cell (DSSC) and DS-PEC literature is that ALD surface treatments are able to uniformly coat the entire interior surface area of a mesoporous metal oxide. However, the AlO_x passivation layer prepared by the ALD protocol used in this study is likely unable to produce a fully conformal coating on the PMPDI loaded throughout the bulk of 4 μm -thick mesoporous SnO_2 . The ALD process, similar to chemical vapor deposition in nature, relies on an efficient transport of vapor-phase precursors to a target surface on which materials are deposited. Unlike flat substrates, three-dimensional (3D) mesoporous substrates require significantly longer time for the precursors to be able to diffuse into the mesopores (i.e., Knudsen diffusion) to generate a fully conformal coating throughout the bulk interior of the mesopores. In our ALD process, the PMPDI-loaded mesoporous SnO_2 was exposed to materials precursors

(either TMA or water) for 1 min during each cycle under dynamic vacuum (i.e., continuous evacuation of the chamber under constant flow of background carrier gas (nitrogen; 20 sccm)). That treatment is not expected to allow diffusion of precursors deep into the bulk of mesoporous SnO_2 film. The resulting AlO_x passivation layer should, then and in turn, be covering mostly only the upper portion of mesoporous SnO_2 film.

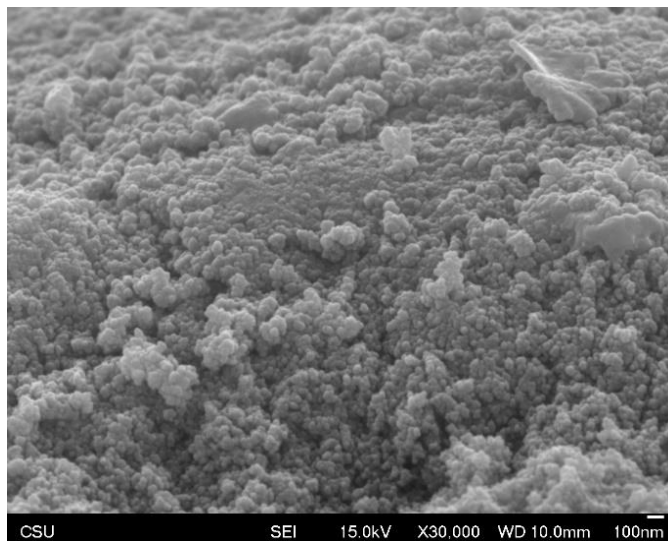


Figure 2.10: SEM image of $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (0.6 nm, 85 °C)/ CoO_y anode taken at 30,000X magnification.

An artistic representation of the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x/\text{CoO}_y$ anode system developed and examined herein was created based on scanning electron microscopy (SEM) imaging of the anodes (Figure 2.10). This rendering (Figure 2.11) is based on a series of SEM images of the anodes, both with alumina (Figure 2.10) and previously published¹⁰, showing the distinctly nanostructured features reflected in this depiction. Understanding the layering and interaction of each component is necessary to accurately examine the kinetics of the system as a whole.

For the thinner AlO_y coatings employed, we illustrate a hypothesized thin surface coating at the outer most surface of the SnO_2 only (Fig. 2.11a). The subsequent application of the CoO_y WOC onto the anode structure likely results in CoO_y directly in contact with PMPDI and SnO_2 , within

the deeper portion of mesoporous SnO_2 film, as opposed to the CoO_y placed on AlO_x overlayer at the upper region of the SnO_2 film. This is consistent with the observed increased charge recombination and, consequently, reduced photocurrent output for the full system with added CoO_y . Attempts to determine the location and prevalence of cobalt using SEM- energy dispersive X-ray spectrometer (EDS) and XPS were unsuccessful due to the very low, catalytic quantities of CoO_y used (for further discussion see S2.5 and S2.7). Although the CoO_y catalyst was not visible by XPS, alumina is present in the anodes according to XPS (Figure S2.4).

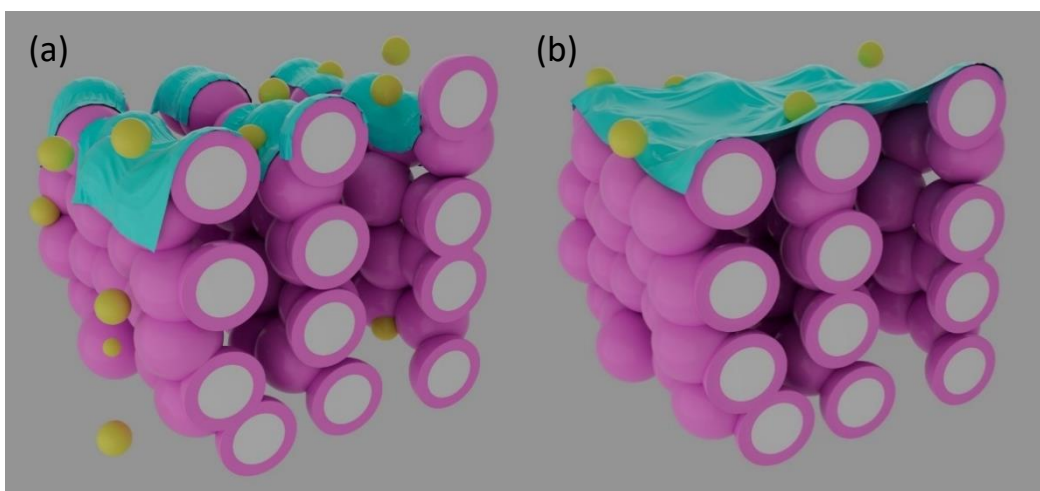


Figure 2.11. Idealized structural models of the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x/\text{CoO}_y$ anode with (a) 0–0.9 nm thick AlO_x layer and (b) 1.3 nm thick or greater AlO_x layer, where SnO_2 is grey, PMPDI is pink, AlO_x is blue, and CoO_y is yellow. Note that in (b) a full, impenetrable coverage by the alumina over the SnO_2 surface is implied, and therefore no yellow CoO_y is shown in the lower part of (b). Structural models are based on SEM imaging of anodes, which showed distinct nanostructured behavior as rendered herein.

As for the 1.3-nm-thick AlO_x layer, the passivation now may be thick enough to more thoroughly cover at least some of the mesopores, more similar to Figure 2.11b than 2.11a, preventing at least some direct contact between SnO_2 and CoO_y as can happen with the ultrathin, 0.6 nm layer for example, so that recombination is not increased (or at least not as much) following the application of CoO_y . But, the thicker AlO_x passivation layer has other effects, as already noted, inhibiting the efficiency of necessary electron transfer from the CoO_y to PMPDI, while also

preventing the full utilization of PMPDI loaded within the bulk of mesoporous SnO₂ film. The net effect of the even modestly thicker AlO_x layer is that the performance of base SnO₂/PMPDI/AlO_x, 0.6 nm thickness AlO_x, anode is overall reduced.

CONCLUSIONS

In the present study we have examined a SnO₂/PMPDI DS-PEC system for photoelectrochemical water-oxidation catalysis where an ultrathin AlO_x passivation layer is added by low-temperature ALD, with and without a CoO_y WOC. The thickness- and deposition-temperature parameters of the ALD were explored with the goal of optimizing the system. The answers obtained to the five primary questions posed at the start of the studies are the following: (i) *yes*, deposition of an ultrathin alumina overlayer applied by ALD on the PMPDI/SnO₂ photoanode can improve the photoactivity and catalytic activity of the system; (ii) *yes*, perhaps surprisingly as one of the more interesting results of the present study, the addition of specifically a ~1-nm-thick AlO_x layer deposited on a *4000 nm (i.e., 4 micron) thick mesoporous* anode system can and does have a positive, 2.5-fold improvement in the steady-state photocurrent with $29 \pm 9\%$ Faradaic efficiency vs the control anode without alumina passivation. Reduced charge-carrier recombination explains the observed effect. Next, (iii) *yes*, layer thickness and deposition temperature of the alumina overlayer are key parameters, a 0.6-nm-thick AlO_x layer deposited at 85 °C providing the best photocatalytic activity in our hands; so that (iv) *yes*, ALD- deposited, ultrathin AlO_x layers is a useful tool to address the carrier recombination in nanostructured/dye systems such as SnO₂/PMPDI DS-PECs. Additionally, (v) *yes*, ALD-deposited AlO_x layer does help support the understanding of the “anti-catalysis” of co-depositing a CoO_y WOC on the SnO₂/PMPDI DS-PECs—specifically the picture of direct CoO_y–SnO₂ contact-mediated recombination—but was unable to improve the photocurrent in a net SnO₂/PMPDI/AlO_x/CoO_y

system. The results document that metal-oxide passivation by low-temperature ALD can be an effective strategy for improving the water oxidation performance of even nanostructured DS-PECs. The results indicate that further optimizing the ALD protocol by tailoring it towards mesoporous structures—for example, by utilizing the ALD-derived infiltration synthesis method^{55,56}—merits experimental testing.

Overall, we find the addition of an optimized *ultrathin* AlO_x layer (0.6 nm thick; deposited at 85 °C) improves the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ system's photoactivity by a factor of up to ~3-fold with reduced recombination. However, the addition of CoO_y still results in a decrease in photoactivity compared to the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ system without CoO_y , but a Faradaic efficiency of oxygen production of ca. 30%. We attribute the lack of a performance enhancement by CoO_y WOC to incomplete coverage of each SnO_2 nanoparticle by the AlO_x . Despite the decrease in photoactivity with the addition of the CoO_y WOC, the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x/\text{CoO}_y$ system yields a higher photocurrent in all cases compared to the original, alumina-free $\text{SnO}_2/\text{PMPDI}/\text{CoO}_y$ system.

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III. UNDERSTANDING THE “ANTI-CATALYST” EFFECT WITH ADDED COO_x WATER OXIDATION CATALYST IN DYE-SENSITIZED PHOTOELECTROLYSIS CELLS: CARBON IMPURITIES IN NANOSTRUCTURED SnO_2 ARE THE CULPRIT²

OVERVIEW

In 2017 we reported a dye sensitized, photoelectrolysis cell consisting of fluorine-doped tin oxide (FTO)-coated glass covered by SnO_2 nanoparticles coated with PMPDI dye and then a photoelectrochemically deposited CoO_x water-oxidation catalyst (WOCatalyst), FTO/nano- SnO_2 /PMPDI/ CoO_x . This system employed nanostructured SnO_2 stabilized by polyethyleneglycol bisphenol A epichlorohydrin copolymer (PEG-BAE) and other C-containing additives based on a literature synthesis to achieve a higher surface area and thus greater PMPDI dye absorption and resultant light collection. Surprisingly, the addition of the well-established WOCatalyst CoO_x resulted in a *decrease* in the photocurrent, an unexpected “*anti-catalyst*” effect. Two primary questions addressed in the present study are (1) what is the source of this “anti-catalyst” effect?, and (2) are the findings of broader interest? Reflection on the synthesis of nano- SnO_2 stabilized by PEG-BAE, and the large, ca. 10:1 ratio of C to Sn in synthesis, led to the hypothesis that even

² This chapter details the preparation, characterization, and photoelectrochemical study of the role of residual carbon impurities in a metal-oxide in a dye-sensitized photoelectrochemical system for water oxidation catalysis. This chapter was published in the Journal ACS Applied Materials Interfaces (Jewell, C. F.; Subramanian, A.; Nam, C.-Y.; Finke, R. G. ACS Applied Materials & Interfaces. <https://doi.org/10.1021/ACSAMI.2C02692>) and has been reproduced with permission. The article is licensed under the American Chemical Society, and further permission requests related to the article should be directed to the ACS. The author of this dissertation, C. F. Jewell, conducted all experiments, with the exception of the atomic layer deposition, and conducted all data analysis. Minor changes to the manuscript have been made to meet dissertation formatting requirements. The supporting information can be found in Appendix II.

the annealing step at 450 °C in of the FTO/SnO₂ anode precursors was unlikely to remove all the carbon initially present. Indeed, residual carbon impurities are shown to be the culprit in the presently observed “anti-catalyst” effect. The implication and anticipated broader impact of the results of answering the two abovementioned questions are also presented and discussed along with a section entitled “Perspective and Suggestions for the Field Going Forward.”

INTRODUCTION

Increasing global demand for energy has led to the declaration that water splitting into hydrogen and oxygen is one of the “Holy Grails” of Chemistry.^{1–7} However, many of the best-performing water oxidation systems use precious rare metals, limiting their commercial viability.^{4,5,8,9} Ideally, the method used to achieve water splitting would involve *earth-abundant materials*.^{8,10–13} In 2014, we published a then novel first-generation photoelectrochemical water-oxidation catalysis (WOC) system consisting simply of the perylene diimide dye, *N,N'*-bis(phosphonomethyl)-3,4,9,10-perylenediimide (PMPDI) spin-coated onto indium tin oxide (ITO) plus a photoelectrochemically deposited CoO_x catalyst, denoted ITO/PMPDI/CoO_x, where anode notation here and in what follows is written in the order of deposition of the indicated components, ITO, PMPDI, and then CoO_x, as shown in Figure 3.1. This first-generation system provided modest photocurrents of ca. 150 μA/cm², but with a faradaic efficiency for O₂ of 80 ± 15% under +0.9 V bias versus Ag/AgCl.¹⁴ However, this deliberately simple initial system was able to harvest only 12% of incident light at the dye’s λ_{max}.¹⁴ Highly relevant for what follows is that addition of CoO_x as a water-oxidation catalyst in this original planar system improved the photocurrent—that is, had the expected

“positive catalyst effect” on water-oxidation catalysis—in every ITO/PMPDI/CoO_x anode examined.¹⁴

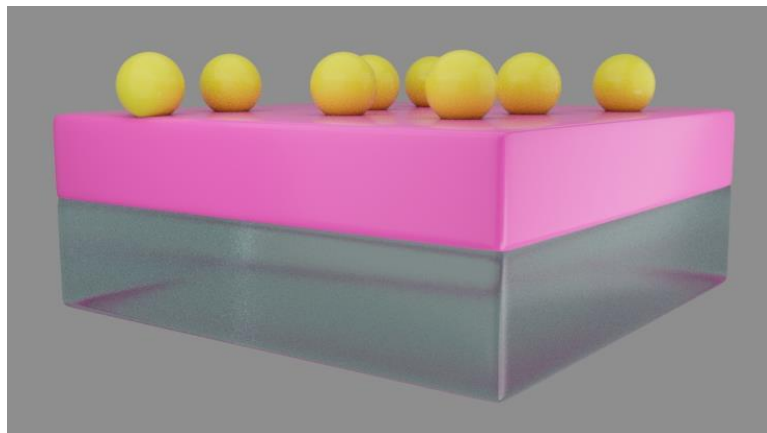


Figure 3.1: Idealized structural model of the ITO/PMPDI/CoO_x anode where ITO is clear, PMPDI is pink, and CoO_x is yellow. Anode notation throughout is written in the order of component deposition, left to right: ITO is used as a base layer, PMPDI is then deposited on the ITO, and then CoO_x is added atop the ITO/PMPDI.

To overcome the low light-harvesting by the planar system, as shown in Figure 3.1, a second-generation, high surface area, nanostructured system was constructed consisting of fluorine-doped tin oxide (FTO)-coated glass covered by SnO₂ nanoparticles coated with PMPDI dye and, then, photoelectrochemically deposited CoO_x water-oxidation catalyst (WOCatalyst), FTO/SnO₂/PMPDI/CoO_x,^{14,15} Figure 3.2. The higher surface area afforded by the nanostructured SnO₂ worked as expected, allowing a higher dye loading as shown visually in Figure 3.3 and a resultant >99% light-harvesting efficiency at the λ_{max} of the dye.¹⁵

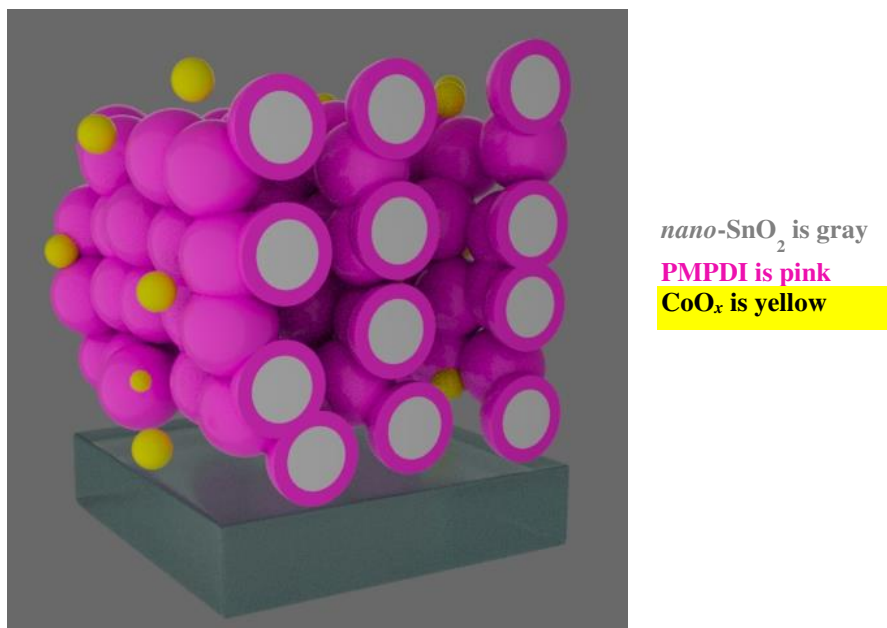


Figure 3.2: Idealized structural model of the FTO/nano-SnO₂/PMPDI/CoO_x anode where FTO is clear, SnO₂ is gray, PMPDI is pink, and CoO_x is yellow. For simplicity, only a small layer of the relatively much thicker, 18 μm , nano-SnO₂ is shown.

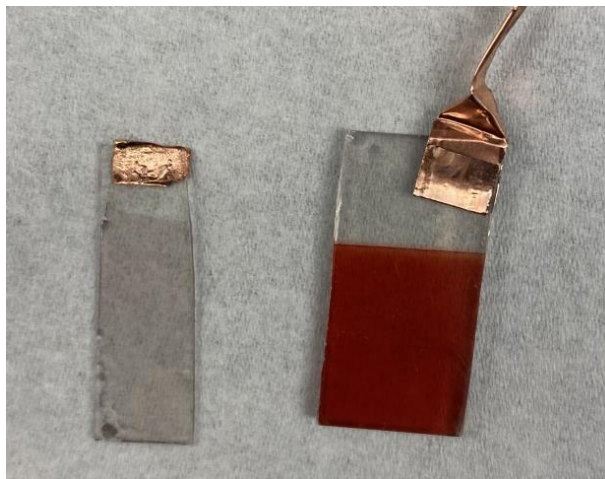


Figure 3.3. Image of the ITO/PMPDI/CoO_x anode (left) and FTO/nano-SnO₂/PMPDI/CoO_x anode (right), where only the bottom two thirds of each anode is dyed. The right-most, FTO/SnO₂/PMPDI/CoO_x anode is obviously darker, clear visual evidence for the larger amount of dye present in the nano-structured, higher surface area, second-generation FTO/nano-SnO₂/PMPDI/CoO_x system.

However, an unexpected, undesired effect of adding the CoO_x WOCatalyst in the nano-SnO₂-based system is that it *lowers* the observed photocurrent, that is, added CoO_x results in an “anti-catalyst”

effect in this second-generation device.¹⁵ This “anti-catalyst” behavior was attributed to the increased charge recombination between photoinjected electrons in the SnO₂ conduction band and accumulated holes in CoO_x catalyst at the SnO₂ surface, that is, trap states at the CoO_x/SnO₂ interface.^{15–17}

Highly relevant here is that others, too, have seen such an “anti-catalyst” effect, specifically Kamire and coworkers in their nano-TiO₂ sensitized by perylene monoimide (PMI) dye using an Ir-dimer-based catalyst¹⁸. Such “anti-catalyst” effects in photoelectrochemical devices illustrate the acknowledged, broader challenge^{13,19} of coupling catalysts to light-absorbing units in ways that minimize charge-carrier-recombination back reactions. Hence, an understanding of the origins and implications of the “anti-catalyst” effect is of fundamental interest and, we will learn, likely considerably broader implications.

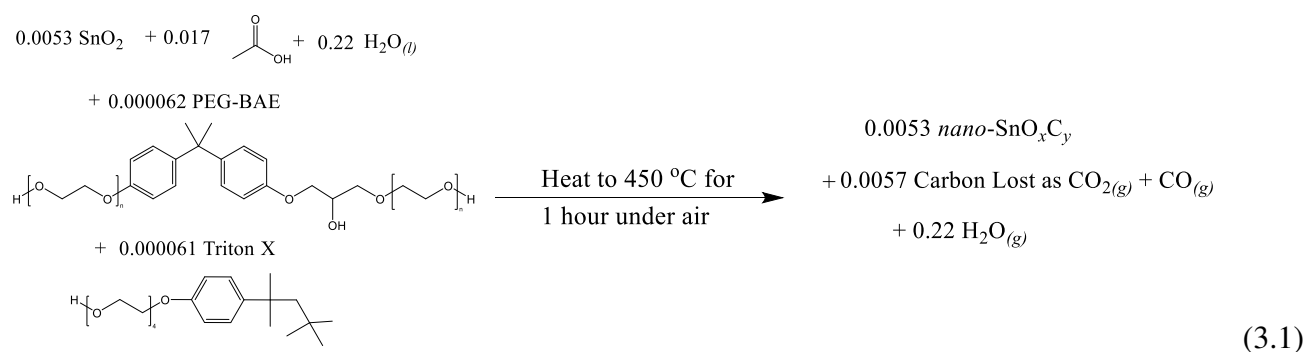
Literature Syntheses of Polymer-Stabilized nano-SnO₂

Nanostructured metal-oxide films, such as the one used herein for SnO₂ in Figure 3.4, have been used in both dye-sensitized solar cells and dye-sensitized photoelectrolysis cells (DS-PECs), and as such, there are numerous preparations for such pastes and film formulations.^{15,18,20–22} As detailed in Figure 3.4, the nano-SnO₂ used in our second-generation DS-PEC was prepared using a commercial SnO₂ nanoparticle powder (NanoArc, Alpha Aesar) wetted with glacial acetic acid and water, then stabilized with the copolymer polyethyleneglycol bisphenol A epichlorohydrin (PEG-BAE) before one drop of Triton X-100 (octyl phenoxy polyethoxyethanol) is added for improved glass adhesion.^{15,23} This nano-“SnO₂” is then doctor bladed onto conductive glass and annealed under air at 450 °C.

An attempt at a balanced stoichiometry for the literature nano-SnO₂ synthesis in so far as possible prior to the present work is shown in eq 3.1 in Figure 3.4. *The resultant value of 10:1 of added carbon to SnO₂ highlights the significant amount of carbon present in the nano-SnO₂ formulation.* Equation 3.1 makes clear that crucial, but unknown, is the amount of carbon, “C_y”, that remains present in the final product initially referred to as nano-“SnO₂”, but hereafter denoted more precisely as nano-SnO_xC_y. Equation 3.2 also makes apparent how *unatom-economical*²⁴ and *ungreen*^{25–27} the literature-based synthesis^{15,23} of nano-SnO₂ is in which 10 equiv of C are added when 0-equiv of C is desired in the resultant product!

A key for what follows is that the thermal annealing in air is implied in the literature, and arguably generally believed, to remove completely the polymer stabilizer and all other traces of carbon, ostensibly as CO₂ shown in eq 3.1. Restated in other terms, in the present nano-SnO_xC_y, is the y really zero as believed in the literature? If not, what, then, is the value of y? What actually is, then, nano-“SnO₂” in terms of nano-SnO_xC_y?

Modified Literature-Based Synthesis^{15,23}



Simplified Stoichiometry for SnO₂ and C-Based Components

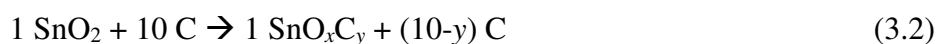


Figure 3.4. Equation 3.1 Shows the Literature Synthetic Procedure For Nano-SnO_xC_y Where First SnO₂, Acetic Acid and Water are Added. Second, PEG-BAE is Added. Third, Triton X-100 is Added. Fourth, the Mixture is Heated to 450 °C in Air and Held at That Temperature for 1 h; This Results in Nano-SnO_xC_y As Well As Various Other Hypothesized Byproducts; Equation 3.2 is a Simplified Version of Eq 3.1, Where the Moles of SnO₂ are Set to 1 (i.e., by Dividing Eq 3.1 through by 0.0053), Thereby Highlighting the 10:1 Carbon to SnO₂ Precursor Ratio in Synthesis

In considering possible origins for the “anti-catalyst” effect of adding the well-established CoO_x WOCatalyst,^{14,15,28–31} it occurred to us that residual carbon not removed by even a 450 °C annealing under O₂ was a possible, if not probable, source of recombination sites in the system. The possibilities for the form(s) of residual carbon range from carbon black, to graphite, to graphene oxide, the later more oxidized form seemingly more reasonable given that the high-temperature annealing takes place under air. Of note here is the carbon removal as CO₂ likely leaves oxygen defects in the nano-SnO_xC_y system as well. The effects of such carbon states on the resulting kinetics^{32,33} of the system are rarely taken into account. A kinetic scheme is presented later on as one illustrative, visual working hypothesis for the photoelectrochemical systems studied herein.

Specific Questions Addressed in This Work and Their Significance.

The specific questions addressed herein are the following: (1) First, is C left as an impurity in nano-“SnO₂”? (2) Second, if so, what then is y in “SnO_xC_y”? And third (3) if y ≠ 0 so that C-impurities are present, then is that C-impurity in turn a source of enhanced recombination in the FTO/nano-SnO₂/PMPDI/CoO_x system? That is, are C-impurities directly connected to the observed “anti-catalyst effect” of added, otherwise effective, CoO_x WOCatalyst? Additionally, we will probe (4) if cleaner atomic layer deposition (ALD) of SnO₂ can be used to deposit lower-C SnO₂ in a, then, SnO₂-modified *planar* version of our WOC system, FTO/ALD-SnO₂/PMPDI/CoO_x? If so, does that low carbon system exhibit a normal “positive catalyst” effect?

Significance of the Present Studies

The significance of the present studies goes considerably beyond the current system given that many nano-metal-oxide syntheses found throughout the literature make use of such organic stabilizers/ thickeners^{15,22,31,34–37} or carbon-based starting materials.³² The organic components of these nano-M_xO_y systems are often ignored as they are either thought to be removed fully through annealing^{15,38}, or if observed, are not taken into consideration of the kinetics and efficiency of those systems.^{32,33} Carbon impurities may in fact be common in nano-M_xO_y systems used in water-oxidation catalysis. Additionally, oxygen, O-atom vacancies in WO₃ are known and have been studied in a FTO/nano-WO₃ system where oxygen-vacancy concentrations have been changed, and the authors then study which charge transfer pathways are most favorable in that FTO/nano-WO₃ system.³² Notably relevant for the present paper, that otherwise excellent, state-of-the-art system and study reports the presence of carbon impurities (in both the text and as seen by X-ray photoelectron spectroscopy (XPS) in the accompanying Supporting Information)³², but then ignore those C-impurities. Those C-based impurities should have been, but were not, considered as an alternative explanation for the observed changes in charge separation and transport seen in the observed kinetics.³²

Additionally, C-based impurities could be a part of the other literature system mentioned earlier that shows an “anti-catalyst” effect of added iridium dimer, a hypothesis that remains to be tested.¹⁸ Overall, the results herein provide a recipe and associated working hypothesis for how to improve the catalyst efficiency in devices that employ metal-oxide nanoparticles involving polymer stabilizers in preparation of the photoelectrochemical device.

EXPERIMENTAL

Experimental conditions used herein are identical to those in our previously published work,^{14,15,31}, unless stated explicitly otherwise. However, key experimental details are provided below as necessary to ensure that the present manuscript is largely self-contained.

Materials. The following starting materials and solvents were used as received to generate buffer solutions: KOH (Fisher, Certified ACS grade, 98.5%, 1.5% water, 0.00028% Fe, and 0.0008% Ni); KH₂PO₄ (Fisher, Certified ACS Grade, 99.3%, 0.0005% Fe); hydroquinone (Aldrich, >99%); and NANOpure water (Barnstead NANOpure ultrapure water system, 18.0 MΩ). NANOpure water was used for all experiments.

Synthesis of Nano-“SnO₂” Following the Literature, Actually Nano-SnO_xC_y. SnO₂ nanoparticle paste was prepared as shown in Figure 3.4 using a modified literature procedure²³ previously worked out for the present system.¹⁵ Using a plastic spatula, 800 mg of white commercial SnO₂ nanopowder (SnO₂, NanoArc® Alpha Aesar, Lot Analysis: 99.6% SnO₂, 47 m²/g specific surface area by BET, 18 nm average particle size, and 6.95 g/cm³ density) was massed into a 20 mL scintillation vial. A Teflon-coated magnetic stir bar and 1.0 mL of glacial acetic acid (ACS grade, Mallinckrodt) were added and the solution was mixed until all the SnO₂ powder was wet; this resulted in the formation of a gray paste. The vial containing this paste was then placed in an ultrasonic water bath (Branson 2510) for 5 minutes. Water, 4.0 mL, was added and the solution was mixed on a stir plate. This paste was then sonicated twice using a QSonica Q125 ultrasonic liquid microprocessor (1/8” probe, held at 80% amplitude) for 5 minutes to form a light gray suspension. Then, 1.10 g of PEG-BAE (Sigma, M_w = 15,000-20,000), which serves as a thickening agent, was added in individual small chunks while stirring over the course of 1 h (S3.1

for reaction equation). New pieces were added only after complete dissolution of the previous addition, by visual inspection, to avoid clumping. Once all the PEG-BAE had been added and dissolved fully, one drop (approximately 20 mg) of Triton X-100 (octyl phenoxy polyethoxyethanol, Sigma) was added with a plastic transfer pipet to increase the adhesion of the paste to the glass substrate. This paste was stirred overnight and then refrigerated in a sealed vial for use over several days with no visual change. Before use, the paste was stirred for approximately 1 h and allowed to reach room temperature.

Planar SnO₂ Preparation by ALD. Ultrathin conformal coatings of SnO_x were prepared using the Cambridge Nanotech Savannah S100 ALD system (base pressure of ~ 0.43 Torr). The deposition temperature was set at 85 °C. The depositions were carried out by sequential exposures to tetrakis(dimethylamido)tin(IV) (TDMASn) (Strem Chemicals) (200 ms) and water vapor (15 ms) with an intermediate purge time of 10 s for both the precursors. To calibrate the thickness of SnO₂ deposited, the deposition cycles were initially chosen as 25, 50, 75, and 100. Spectroscopic ellipsometry was used to calibrate the SnO_x thickness per ALD cycle using Si control substrates and found a linear growth rate of 0.152 nm per cycle (Figure S3.1 and Table S3.1). The number of ALD cycles varied between 4 and 122 to deposit SnO_x with thickness ranging from 0.6 to 18.0 nm as desired.

Synthesis of PMPDI dye, and the Deposition of SnO₂ Anode and CoO_x WOCatalyst. All synthetic and manufacturing details for PMPDI dye can be found in our previous publications.^{14,15} Briefly, the anodes are composed FTO-coated glass as a transparent current collector, covered by SnO₂, either a mesoporous nano-“SnO₂” or SnO₂ by ALD. The SnO₂ coated anodes were then sensitized with PMPDI and CoO_x was photoelectrochemically deposited as the water oxidation catalyst. All fabricated photoanodes have SnO₂ films with “2-Scotch” layer thickness conditions¹⁵

where PMPDI dyes were loaded for 24 h at 95 °C from a saturated solution of fully protonated PMPDI in water.¹⁵ CoO_x WOCatalyst was added to photoanodes by photoelectrochemical deposition.^{14,15} The anodes (SnO₂/PMPDI) were submerged in a solution of pH 7, 0.5 mM Co(NO₃)₂ and 0.1 M potassium phosphate buffer (KPi) and held at +0.2 V versus Ag/AgCl under 1 sun illumination for 3 min.¹⁵ Anodes were then rinsed with water for 30 s and allowed to air dry.

Photoelectrochemical Testing. All photoelectrochemical experiments were carried out in a previously described^{15,31} custom two-compartment Pyrex cell consisting of a working compartment (1 × 1.5 × 1.5 cm³, 5 ml) and an auxiliary compartment separated by a medium porosity glass frit. Experiments were conducted using a CH Instruments CHI-750D bipotentiostat, a Pt wire counter electrode and a Ag/AgCl (3 M NaCl, +0.215 V versus normal hydrogen electrode) reference electrode. The reference electrode was positioned in the working compartment in close proximity to the anode surface and the counter electrode was placed in the auxiliary compartment. The anode was clamped with an alligator clip to the front wall of the working compartment with the nonconductive glass side pressed flush to the cell wall. Then both compartments of the cell were filled with ca. 5 mL electrolyte (pH 7, 0.1 M KPi buffer), sufficient to cover the film. The anode was illuminated from the substrate side using a 65 W xenon arc lamp (PTO model A1010), which was powered using an OLIS XL150 adjustable power supply. The light passed through a bandpass filter (315–710 nm, Thorlabs KG3, FGS900S) and an ultraviolet (UV) filter (400 nm long-pass, Thorlabs FGL400S) before reaching the anode. The power density of the light was adjusted to reflect the visible region of the airmass 1.5 global (AM 1.5G) spectrum.¹⁵ In the experiments in which transients (interrupted illumination) were used, a manual shutter was used to block the light.¹⁵

Each anode was tested with a series of electrochemical experiments in the order detailed below. First the cell was allowed to short-circuit in the dark for 60 s to depopulate the electrons from SnO₂ sub-bandgap states.¹⁵ Then the open-circuit potential, V_{oc} , was measured versus the Ag/AgCl reference electrode for 90 s in the dark and then again under illumination. Next, a photocurrent transient experiment was performed in which the anode was held at +0.2 V versus Ag/AgCl for 300 s with 30 s light/dark transients throughout. The anode was then allowed to short-circuit in the dark for 60 s, and the V_{oc} in both the dark and light was remeasured. Then, the current-voltage (i - V) photocurrent transient experiment was performed. The voltage was scanned from -0.2 to +1.0 V versus Ag/AgCl with a 10 mV/s scan rate and 5 s light transients. Each experiment was reproduced a minimum of three times with three separate, independent anodes produced under identical conditions. All figures and values reported herein are representative of the photoactivity of the system indicated. Care was taken to ensure that the reported results are reproducible across separately made anodes and not due to a defective anode or otherwise irreproducible sample or result.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA 2950 thermogravimetric analyzer under air flow. The heating regime used mimicked the above nano-“SnO₂” synthesis exactly; the temperature was ramped from 20 °C to 450 °C, ramping 20 °C /min, and held for 1 h. A platinum TGA pan was used to hold the sample.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) was carried out using a PE-5800 series Multi-Technique ESCA XPS system where a Al K α monochromatic source operating at 350.0 W was used for all XPS experiments. High resolution (HRES) scans were carried out for all elements present in the initial survey scan at a minimum of three spots across the sample surface for 30 minutes apiece.

To fit the data, CASAXPS software was used to analyze the data. Quantification results for each element were tabulated using an average of each replicate scan. Consistent with both the literature method of XPS fitting and ensuring the self-consistency across fits, HRES spectra were calibrated to a 285 eV aliphatic carbon peak.^{39,40} Sputtering was carried out using Ar⁺ ions at 5kV for 1 minute over a 3 x 3 mm² area. The area analyzed by XPS was taken from the center of the sputtered region.

Scanning electron microscopy. Scanning electron microscopy (SEM) images were taken for nano-“SnO₂”/PMPDI and ALD-SnO₂ anodes using a JEOL JSM-6500F field emission scanning electron microscope (FESEM), using 15 kV accelerating voltage and 10 mm working distance. Energy dispersive X-ray spectrometry (SEM-EDS) data were collected using an Oxford Instruments energy dispersive X-ray spectrometer. Qualitative and quantitative elemental analyses were carried out using Oxford Aztec software. A nano-“SnO₂”/PMPDI anode was cracked in half and was then coated in 10 nm of gold to examine the cross section. Of note, the sample had to be oriented at a slight angle off of vertical.

Oxygen Detection. Oxygen yield was experimentally measured using the generator–collector (G-C) technique detailed elsewhere.^{15,41–43} Briefly, photoanode ‘generators’ were sandwiched with an FTO “collector”,¹⁵ separated by a Parafilm spacer. The resultant G-C cell was placed in the previously detailed working compartment with the generator side flush to the wall of the cell nearest the incoming light. The cell was filled with pH 7, 0.1 M KPi buffer, approximately 10 mL which was degassed with Ar for a minimum of 60 min. Current was measured at both the generator and collector electrodes, which were held at +0.2 V and –0.65 V versus Ag/AgCl, respectively. The current was collected for 300 s in the dark, 300 s in the light, then 300 s in the dark to ensure all oxygen diffused across the two electrodes and current attributable to oxygen production was

detected. Control experiments with FTO/CoO_x anodes were used to determine the collection efficiency of the sandwich configuration¹⁵ and used to calculate the O₂ yield and Faradaic efficiency of each photoanode.

RESULTS AND DISCUSSION

In-House Nano-“SnO₂” Synthesis and Carbon Impurities

As detailed in the Experimental Section, current nano-“SnO₂” synthesis (really nano-SnO_xC_y synthesis, *vide infra*) relies heavily on a large excess of organic stabilizers, resulting in a final paste with a formulation of ca. 11 wt % SnO₂, 15 wt % acetic acid, 17 wt % PEG-BAE, and 57 wt % water,¹⁵ Figure 3.4 1, *vide supra*. As Figure 3.4 points out, this results in a hugely atom-uneconomical ~10:1 molar ratio of C-to- SnO₂ in the initial paste—10 moles of C-impurity versus 1 mole of the desired SnO₂. To attempt to remove the carbon, once the paste is deposited on the conductive glass the literature synthesis sinters the anodes under air in a furnace in which the temperature is gradually increased (ca. 20 °C/min) to 450 °C; the temperature is then held at 450 °C for 1 h before very gradual (less than 1 °C/s) cooling back to room temperature. During this carbon-removal sintering process (i.e., attempted full removal of the PEG-BAE, Triton X-100, and acetic acid), a carbon-free, pure nano-“SnO₂” has been thought to be formed.⁴⁴ However, the specific literature hypothesis that $y = 0$ for the SnO_xC_y product has not been quantitatively tested until now.

Post some reflection, we hypothesized that carbon-impurities remain in the nano-“SnO₂” prepared by the literature route^{15,23} and that this residual carbon is what is causing the observed, decreased water oxidation performance and the “anti-catalyst” effect.¹⁵ As a test of this hypothesis and the specific question of “is y in SnO_xC_y in fact $\neq 0$?”, an initial control experiment of a TGA

on just the PEG-BAE organic stabilizer was run in which the TGA conditions were set to mimic the 450 °C in the air annealing method used on the anodes, Figure 3.5. After the full TGA schedule of 450 °C for 1 h, *3.1% of the PEG-BAE remained*, indicating that not all the carbon is removed during at least this particular sintering process on a platinum TGA pan, resulting visually in a black powder as expected for elemental C. Residual carbon in a, then, FTO/nano-SnO_xC_y/PMPDI/CoO_x photoelectrochemical device is particularly concerning as the CoO_x catalyst deposition is accomplished photoelectrochemically, implying that the expected high electrical conductivity of residual carbon could play a significant role in the placement and properties of the CoO_x WOCatalyst.

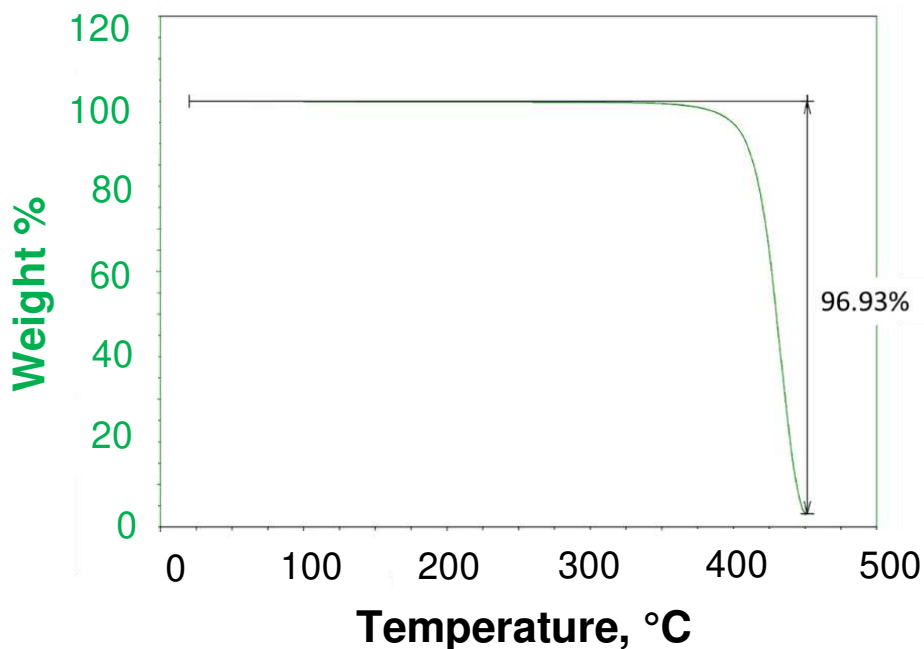


Figure 3.5. TGA of 17.56 mg of PEG-BAE stabilizer placed in a platinum TGA pan. Ramped from 20 °C to 450 °C, ramping 20 °C/min, and held 1 h. This procedure mimics the typical sintering conditions used on the nano-SnO_xC_y for anode production. After 1 h at 450 °C 3.1% of the PEG-BAE, 0.54 mg, remained, indicating that all the C present initially is *not* removed by this thermal treatment.

A second control experiment was carried out in which, now, the nano- SnO_xC_y paste was sintered at 450 °C for varying amounts of time: unsintered (0 h), sintered traditionally for 1 h, and sintered for 7 days. Each of these pastes were then examined using XPS, Table 3.1 and S3.3. The unsintered paste had the expected significant amount of carbon, ca. 66%. In both samples sintered for either 1 h or 7 days, a significant amount of carbon remained, approximately 11%, in the nano- SnO_xC_y film for both the samples regardless of the 1 h versus 7 days of sintering. Noteworthy is that sintering the nano- SnO_xC_y paste for even 7 days does not remove more C within experimental error in comparison to the traditional 1 h at 450 °C. No matter how long we sinter at 450 °C, a significant amount of carbon, roughly 11% C, remains in the sample. Of note here is that the difference between 69% and 11% (or at most ~15% from the last entry in Table 3.1) is far greater than any error due to adventitious carbon⁴⁵ in the experiment.

Table 3.1. XPS Characterization of Sintered nano- SnO_xC_y under several conditions

XPS of nano- SnO_xC_y	unsintered (0 h) ^a	sintered 1 h ^a	sintered for 7 days ^a
weight percent C	65.5 ± 5.0	11.1 ± 0.3	13.6 ± 1.3

^a Three independent anodes, analyzed at three spots on each anode.

As a control, a more bulk-sensitive (i.e, less-surface-sensitive) technique, SEM-EDS, was also used to verify the amount of carbon in the normal, 1-hr sintered sample (i.e., in an attempt to decouple any potential adventitious surface-adsorbed carbon, a part of most XPS samples, from the amount of carbon remaining in the sintered nano- SnO_xC_y). Specifically, SEM-EDS was carried out on the cross section of a deliberately cracked nano- SnO_xC_y anode, Figures 3.6a, b. *There is clearly carbon present throughout the cracked anode*, indicating that there is incorporation of the carbon throughout the nano- SnO_xC_y , and indicating that the majority of the ~11% C in the standard, 1 hr sintered samples is not from any source of adventitious carbon. Moreover, a clear distinction

in the amount of carbon present can be seen where the FTO glass is, indicating that the carbon in the bulk nano-SnO_xC_y sample is well beyond the background of any / all types of adventitious carbon. Moreover, *by EDS, the carbon was found to be 10.8 ± 0.8 wt %* in sections of the nano-SnO_xC_y anode, *quantitatively comparable to the 11.1 ± 0.3 wt % of carbon by XPS*. The EDS and XPS results in turn yield $y = 0.22$, that is, nano-“SnO₂” is really nano-SnO_xC_{0.22}. Noteworthy here is that the ~11% residual carbon in the nano-SnO_xC_y is higher than the 3.1% residual carbon in the TGA experiment on just the PEG-BAE stabilizer, consistent with the expectation that carbon in SnO_xC_y should be—and experimentally is—harder to remove.

Hence, our first three specific questions have been answered: (1) yes, C is left as an impurity in nano-“SnO₂”, that is, $y \neq 0$ in “SnO_xC_y”; (2) $y = 0.22$, or ~11 wt. %, even in the XPS control of 7 days of 450 °C sintering in air of nano-SnO_xC_y; (3) yes, a viable hypothesis is, then, that residual C is likely influencing the charge-transfer kinetics of the FTO/nano-SnO_xC_{0.22}/PMPDI/CoO_x photoelectrochemical WOC system, for example as carbon-defect-based trap states. It follows that the nano-SnO_xC_{0.22}-based system needs to be further examined to see whether it exhibits the observed, “anti-catalyst” effect post adding the well-established, normally “positive” WOCatalyst CoO_x.

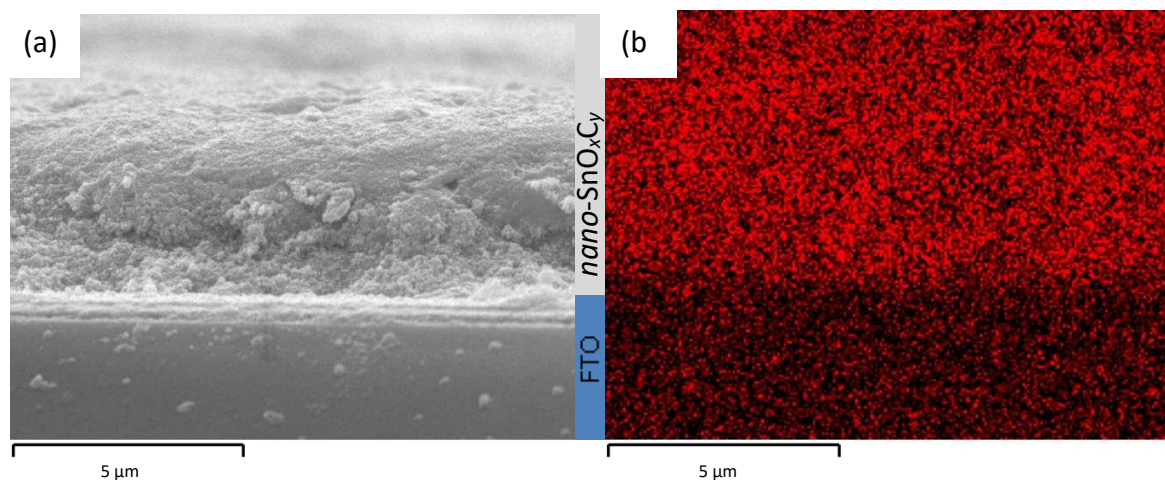


Figure 3.6: (a) SEM image of a nano-SnO_xC_y anode taken at 30,000X magnification. Image is a profile of the cross section of the anode after deliberately cracking. The FTO glass is clearly visible at the bottom of the SEM image of the cross section for reference and perspective. (b) EDS image of the same anode in the same orientation showing only the distribution of carbon across the sample in red. For clarity at the left of figure 3.5b (i.e., in between the Figure 3.5a and 3.5b) a bar labeling the areas of the cross section is included between the two figures where the blue represents the FTO conducting glass and the light gray is the nano-SnO_xC_y.

Testing the Carbon Impurity Hypothesis by Changing the Carbon Level

To probe the leading hypothesis that carbon impurities in the nano-SnO_xC_{0.22} are the source of the “anti-catalyst” inefficiency in our nanostructured, nano-SnO_xC_{0.22}-based anodes, anodes with differing amounts of carbon present were prepared and then tested. In order to best replicate the (precisely unknown) form(s) of carbon present in the nano-SnO_xC_y, the amount of PEG-BAE organic stabilizer used in the synthesis was altered. Specifically, using an otherwise identical synthesis, anodes with half as much PEG-BAE and, then, additionally twice as much PEG-BAE added into the SnO₂ paste as the traditional synthesis were fabricated and tested (denoted as 0.5 equiv PEG-BAE anodes and 2 equiv PEG-BAE anodes, respectively). Importantly, SEM-EDS characterization of the carbon in the 0.5 equiv PEG-BAE anodes and for the 2 equiv PEG-BAE anodes verified the synthetic strategy by showing 7.8 ± 0.8 and 26.7 ± 0.7 wt %, respectively (Figure S3.3), in the respective anodes.

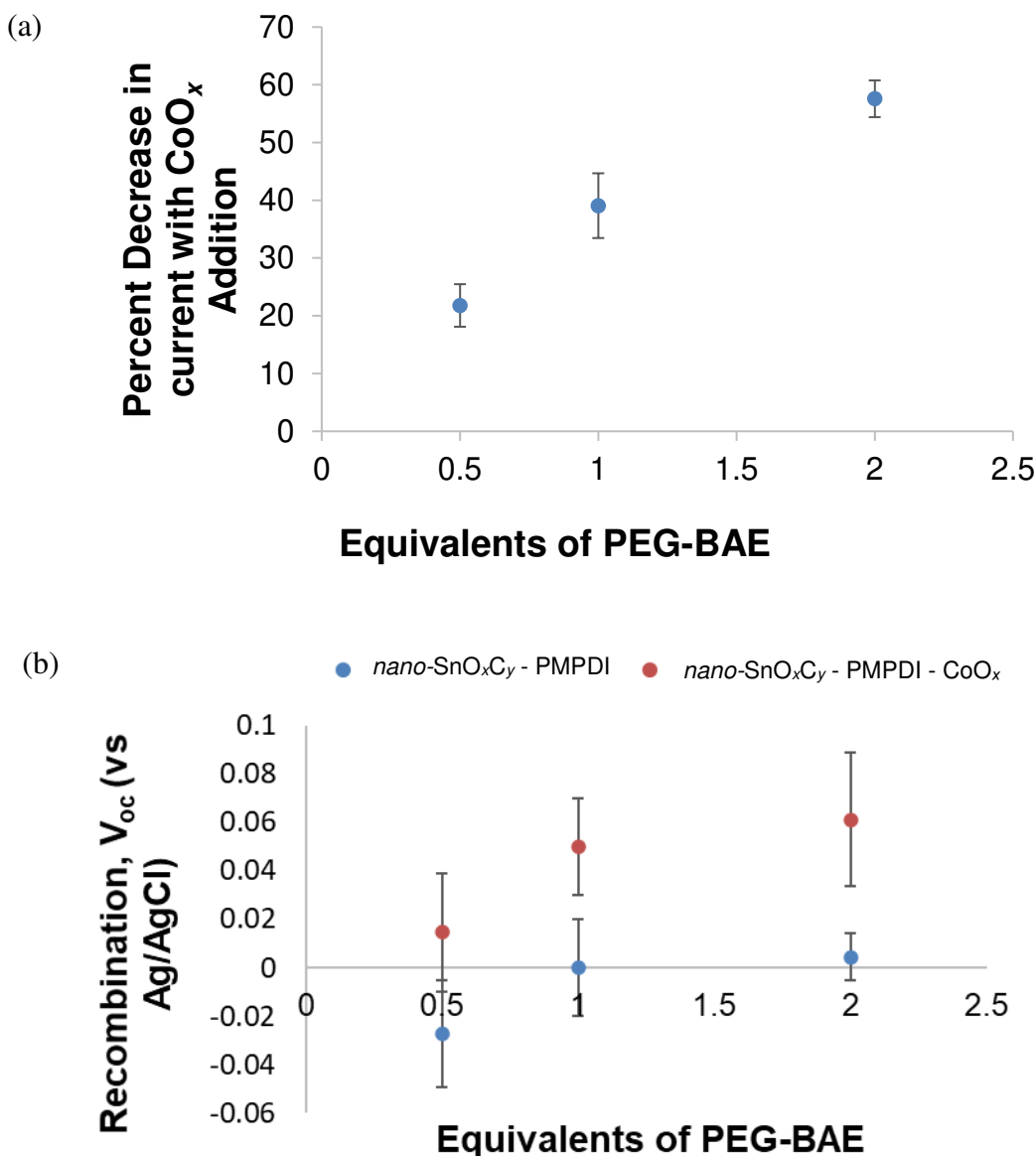


Figure 3.7. (a) Percent loss of the steady-state photocurrent with the addition of CoO_x catalyst at differing amounts of PEG-BAE addition where 1 equiv is the amount added in a typical, traditional synthesis. (b) V_{oc} versus Ag/AgCl reference electrode in a half-cell setup for nano- SnO_xC_y /PMPDI (blue) and nano- SnO_xC_y /PMPDI CoO_x (red) anodes at differing amounts of PEG-BAE addition where 1 equiv is the amount added in a typical, traditional synthesis. In this case, $V_{oc} \approx E_{F,n}$, the quasi-Fermi energy of electrons in the SnO_2 sub-bandgap states.^{15,31}

In each case, the addition of the CoO_x catalyst once again resulted in a decrease in the steady-state photocurrent for all the used PEG-BAE amounts (Figures 3.7a). Significantly, the experimentally observed photocurrent decrease *correlates directly with the amount of carbon*,

added initially as PEG-BAE, in the nano-SnO_xC_y: the anodes with only 0.5 equiv of PEG-BAE exhibit a *smaller decrease* in photocurrent with the addition of the catalyst, $22 \pm 4 \%$, while the anodes with 2 equiv PEG-BAE have a *larger decrease* in photocurrent, $58 \pm 3\%$. These data constitute arguably prima facie evidence for a direct connection between the amount of carbon impurity present in the nano-SnO_xC_y and the degree of “anti-catalyst” behavior following the addition of the CoO_x WOCatalyst.

Also noteworthy here *is the fact that each anode, regardless of amount of PEG-BAE added, was found to have the same concentration of dye within experimental error by UV visible spectroscopy* (Figure S3.4). As such, those data rule out the otherwise plausible alternative hypothesis that the “anti-catalyst” effect is due to differing degrees of *overall binding* between the PMPDI dye and the metal-oxide surface³⁶ (still due, in this alternative hypothesis, to the presence of carbon). However, note here that we cannot say that different dye morphologies or some other different structural parameter does not result in the FTO/nano-SnO_xC_{0.22}/PMPDI/CoO_x system due to the carbon-impurity. Indeed, a rational probe of the mechanism(s) behind the effect(s) of carbon impurities requires first and at a minimum the synthesis and characterization of a presently unknown, pure nano-“SnO₂”. Hence, deeper insights into the role(s) of carbon impurities will have to be the focus of needed future efforts and studies. The main message of the present work is “avoid carbon impurities” until and unless you are sure you want them in your particular system.

Open-Circuit Potential Data, V_{oc}.

To better understand the role of the carbon impurity in FTO/nano-SnO_xC_y/PMPDI/CoO_x systems, recombination was studied. To estimate the relative amount of recombination, the open-circuit potential (V_{oc}) of the anode under illumination was measured for anodes prepared from

different starting amounts of PEG-BAE and, hence, differing amounts of carbon, y , in the nano- SnO_xC_y (Figure 3.6b).^{15,31,46} V_{oc} values reflect the quasi-Fermi energy of electrons ($E_{\text{F,n}}$) in the nano- SnO_xC_y substrate with respect to a Ag/AgCl reference electrode potential.^{15,31,46} Steady-state charge-carrier concentration determines the V_{oc} , meaning the relative rates at which electrons are injected from the photoexcited dye to SnO_2 versus the rate of depopulation of the SnO_2 via recombination set that in/out equilibrium. Experimentally, in anodes with half as much PEG-BAE *no significant increase in recombination was observed with the addition of catalyst*, Figure 3.7b. However, in anodes prepared under normal, 1 equiv, PEG-BAE addition and with 2 equiv of PEG-BAE *an increase in recombination with the deposition of CoO_x catalyst occurs*, Figure 3.6b. With higher, 1 equiv amounts of PEG-BAE leading to higher levels of C-impurities, there is also an increase in recombination compared to anodes with less PEG-BAE, Figure 3.7b.

The V_{oc} data in Figures 3.7a,b provide strong, if not compelling, evidence that the carbon impurity from the organic stabilizer in the resultant nano- SnO_xC_y plays a key role in determining the recombination kinetics. Altering the concentration of the C-impurity significantly shifts the relative ratios of at least some kinetic pathways within the charge-carrier kinetics. The origins of the “anti-catalyst” effect are thereby traced to the presence of C-impurity. The evidence is compelling that if carbon impurities are present, then their role(s) in the charge-carrier kinetics of the system must be included in at least the present system and, by implication, in the future discussions of DS-PEC systems more generally. The fact that the C-impurity comes from an *unatom-economical*²⁴ and *ungreen*^{25–27} literature synthesis, that starts out with a 10:1 C to SnO_2 ratio in a synthesis that is aimed at a 0:1 ratio of C to SnO_2 in the product, makes apparent the future goal of designing syntheses of nanostructured M_xO_y stabilized by a minimum of presumably

non-polymeric, ideally readily removable stabilizing ligands. Just such studies aimed at purer nano-SnO₂ are in progress.

Testing the Effect of Added C-Black

As one additional test of the effects of deliberately added carbon, anodes were produced with the direct addition of carbon black as a well-known, specific type of carbon. Recombination was found to significantly increase with the inclusion of carbon black at both two and five equiv of added carbon black (Figure S3.6). Hence, these experiments with added C-black provide additional evidence for and verification of the data and conclusions from the above, varied PEG-BAE equivalents, study. Additionally, as in anodes in which carbon black is added, the same trends are observed as in anodes with PEG-BAE addition, data that argue any changes in the oxygen concentration that may arise with PEG-BAE variation is not a dominant effect in this system. In total, the results presented herein provide strong support for the hypothesis that carbon impurities lead to enhanced recombination in at least the present FTO/SnO_xC_y/PMPDI/CoO_x WOC system and almost surely in other, related systems as well.

Kinetics Scheme for the FTO/SnO_xC_y/PMPDI/CoO_x System as a Working Hypothesis Going Forward

In order to better visualize the impacts of carbon impurities on the charge-transfer pathways throughout the system, a kinetics scheme for the SnO_xC_y/PMPDI/CoO_x system was constructed as a working hypothesis for going forward, Figure 3.8.

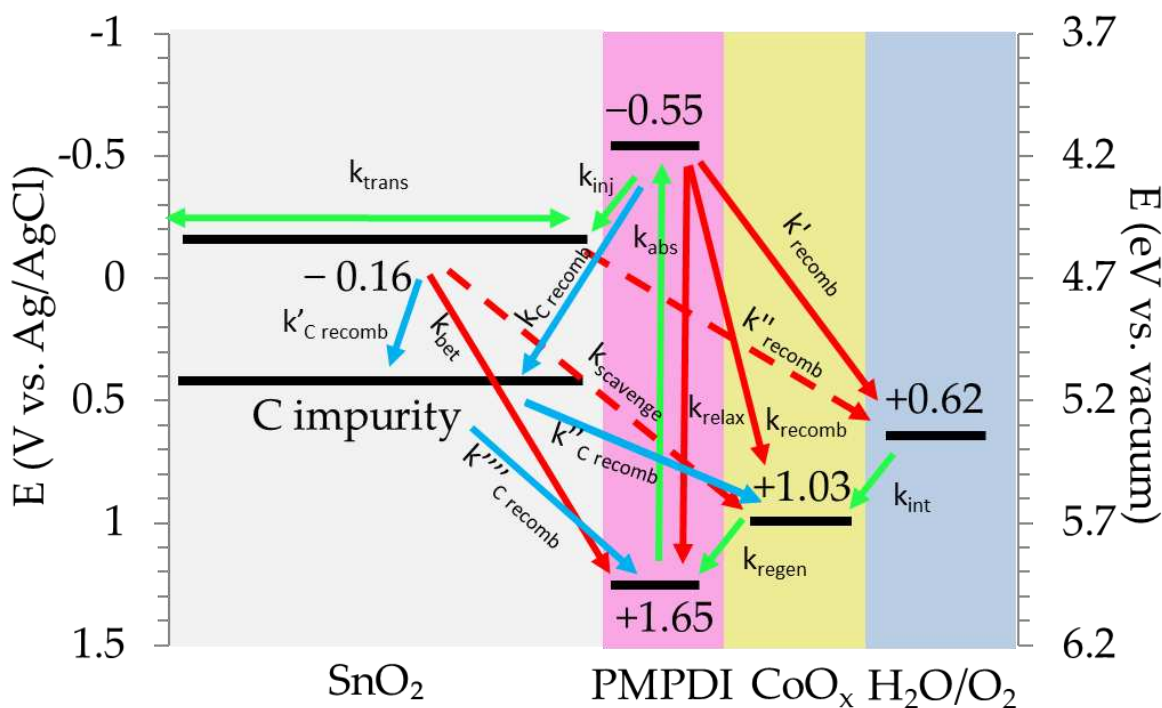


Figure 3.8. Hypothetical Kinetics Scheme of the SnO_xC_y/PMPDI/CoO_x System Intended as an Illustrative Working Hypothesis.^a

^aSnO₂ is white, PMPDI is pink, and CoO_x is yellow. The blue arrows indicate possible recombination pathways from any carbon defects present in “SnO_xC_y” whereas green arrows indicate idealized pathways for charge transfer in the water-oxidation catalysis. Red arrows indicate loss of efficiency in the form of charge-carrier recombination. All other potential impurities and defects, including O-vacancy defects³², are omitted from this scheme for the sake of simplicity, but oxygen-defects are also possible and might even impact carbon-based recombination.

Kinetic pathways are identified using k_{trans} , k_{scavenge} , k_{inj} , k_{recomb} , k_{abs} , k_{bet} , and k_{relax} , indicating, respectively, electron transfer, scavenging, injection, recombination, absorbance, back electron transfer, and relaxation. Inherent charge-recombination pathway rate constants are shown in red, whereas the new pathways due to C-based recombination are shown in blue. For simplicity the carbon impurities are depicted as a single state, although realistically multiple different potentials at points where the carbon impurities sit are likely, approaching a band of potentials for carbon impurity and a “dispersive kinetics” type of situation.^{47,48} The addition of charge transfer

pathways, particularly recombination, involving carbon impurities shows the numerous pathways in which carbon impurities can alter the charge-transfer kinetics. Simply omitting the blue arrows from Figure 3.8 provides an illustration of a hypothetical system free of impurities and defects. Future fast spectroscopic kinetics study and data will be needed to provide evidence for or against the specific pathways postulated in Figure 3.8 and their relative rate constants.

Further Test of the C-Impurities and Thereby Enhanced Recombination Hypothesis: Photocurrents from SnO₂ Films by ALD in the System

A prediction from the “C-impurities cause enhanced recombination” hypothesis and from the kinetics shown in Figure 3.8 is that the addition of a lower C-content SnO₂ layer *in the planar system* might be able to overcome the “anti-catalyst” effect and might even exhibit a positive effect upon the addition of CoO_x. ALD can provide films with a low defect density and is a deposition method able to produce a better controlled system with fewer impurities.^{49–52} Hence, SnO₂ deposition by ALD was employed to generate what proved to be the desirable, lowered-carbon form of SnO₂.⁵³

Specifically, ALD-deposited SnO₂ was added in a planar layer to yield FTO/ALD-SnO₂/PMPDI, as detailed in the Experimental Section. Although anodes for WOC testing used 5 nm thick layers of ALD-SnO₂, a much thicker, 18 nm, layer of ALD-SnO₂ was deposited and utilized to examine the amount of carbon impurity (i.e., with the goal of emphasizing carbon in the bulk material and not surface-adsorbed adventitious carbon). SEM-EDS examination of this FTO/ALD-SnO₂ yielded 1.68 ± 0.02 wt. % carbon. The surface of the SnO₂ deposited by ALD showed $5 \pm 3\%$ carbon by XPS, while mild sputtering to remove adventitious carbon from normal

room air and vacuum grease⁴⁵ showed ca. $3 \pm 3\%$ carbon by XPS. Hence, there is significantly less carbon in the ALD-SnO₂ than that in the nano-SnO_xC_y both by XPS and SEM-EDS.

The photoelectrochemical performance of the FTO/ALD-SnO₂(5 nm)/PMPDI anodes, using 5 nm thick layers of ALD-SnO₂, was studied in pH 7 buffer. As the SnO₂ deposited by ALD is planar, the electrochemically-active surface area is much smaller than that for the three-dimensional nano-SnO_xC_y, and, as such, the expected photocurrents are lower than that in the nano-SnO_xC_y-based system. Hence, hydroquinone (H₂Q) was examined as before^{14,15} as a sacrificial reductant that undergoes a kinetically facile, $2e^-$ and $2H^+$ oxidation (i.e., one closer to the $4e^-$ and $4H^+$ required for water oxidation^{4,15,54} and, therefore, a better model for water oxidation catalysis than common, sacrificial reductants such as $K_4Fe^{II}(CN)_6$ ^{14,55,56} and its $1e^-$, $Fe^{II/III}$ redox couple). Photocurrent transients were carried out on ALD-SnO₂ anodes with and without catalyst in the presence of H₂Q (Figure 3.9).

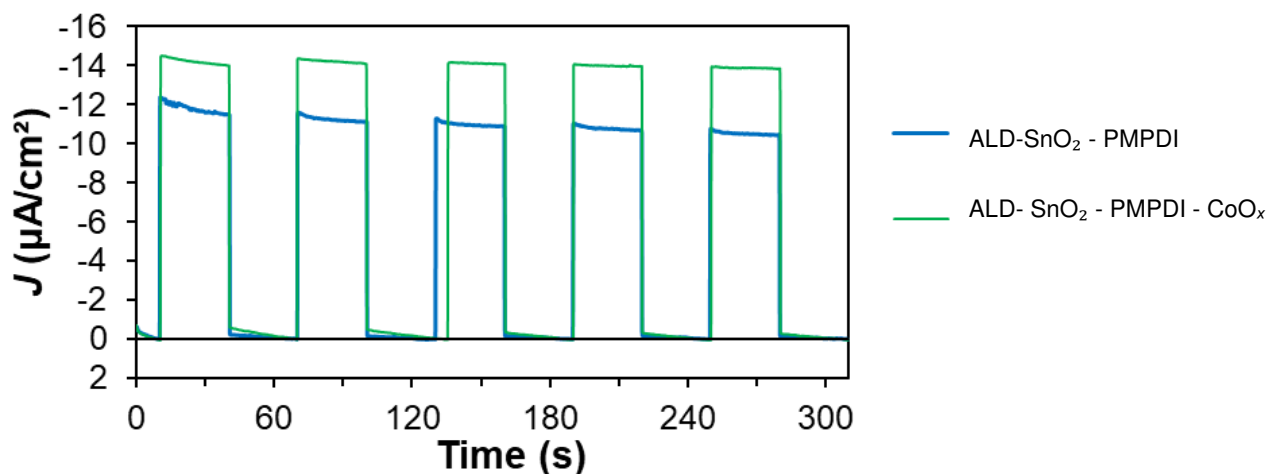


Figure 3.9. J - t transients in the presence of 20 mM H₂Q sacrificial reductant, with background dark current subtracted, at +0.2 V versus Ag/AgCl in pH 7, 0.1 M KPi buffer with 30 s light/dark transients where blue is FTO/ALD-SnO₂(5 nm)/PMPDI, and green is FTO/ALD-SnO₂(5 nm)/PMPDI/CoO_x.

Significantly, the observed photocurrents *increased* ca. 31% with the addition of CoO_x, as shown in Figure 3.6, from ca. -10.5 to -13.8 $\mu A/cm^2$, indicating that CoO_x deposition onto the ALD-SnO₂

coated with dye yields the desired *positive effect* of adding the CoO_x WOCatalyst. In short, reducing the carbon impurity even further, as low as currently feasible using ALD- SnO_2 in the planar FTO/ALD- SnO_2 (5 nm)/PMPDI/ CoO_x system, is able to overcome the “anti-catalyst effect”. These results therefore confirm and compliment those seen with the nano- SnO_xC_y system. Overall, the results to this point provide strong support for carbon impurities as the culprit in enhancing recombination in the nanostructured FTO/ SnO_xC_y /PMPDI/ CoO_x system.

Nano- SnO_xC_y /ALD- SnO_2 /PMPDI

In an attempt to find a sort of goldilocks version of the SnO_2 systems in which the increased surface area and hence enhanced dye absorbance of the nano- SnO_xC_y was somehow balanced by the decreased carbon impurities of ALD- SnO_2 , a “double SnO_2 ” system combining both forms of SnO_2 was tested. Specifically, anodes consisting of nano- SnO_xC_y were coated with a relatively thick, 18 nm of ALD- SnO_2 , with dye and then CoO_x catalyst was deposited. This thick, 18 nm, layer of SnO_2 was chosen as a compromise to coat at least a significant part of the nano- SnO_xC_y without the loss of too much of the higher surface area provided by the nano- SnO_xC_y . Again, the amount of dye on the nano- SnO_xC_y /ALD- SnO_2 /PMPDI was found to be comparable to that of the nano- SnO_xC_y /PMPDI anodes by UV-vis, suggesting that PMPDI binds to the SnO_2 with a similar affinity on the nano- SnO_xC_y /PMPDI and on the thin, non-nanostructured, ALD- SnO_2 (Figure S3.4).

The resultant photocurrent transient data showed, however, that even with an 18 nm coating of ALD- SnO_2 the addition of the catalyst *still decreases the photoactivity* (Figure S3.8), that is, still shows the “anti-catalyst” effect post adding CoO_x . While it is conceivable that an even thicker ALD- SnO_2 layer *might* work better, the results suggest that, instead, future research efforts would

be better placed toward developing superior, *carbon-free syntheses of SnO₂ and other M_xO_y nanoparticles*. As already noted, such needed efforts are in progress.

Demonstration of Water Oxidation Catalysis by the ALD-SnO₂/PMPDI/CoO_x Anodes

Actual water oxidation for the ALD-SnO₂/PMPDI/CoO_x anodes, which were found to display improved photocurrents with catalyst addition in hydroquinone (Figure 3.9), *vide supra*, was measured in the absence of any sacrificial reagent as a control to ensure that the photocurrent observed in the hydroquinone system is representative of the anode's WOC properties (Figure 3.10). *Importantly, the addition of CoO_x catalyst showed a positive water-oxidation catalysis response, improving the photocurrent.* Although challenging due to the expected low, $\mu\text{A}/\text{cm}^2$ range, photocurrents for the planar system, Faradaic efficiencies for water oxidation catalysis could be calculated and hence were also measured for the ALD-SnO₂/PMPDI/CoO_x system using the generator-collector method.^{15,43} The observed Faradaic efficiencies were found to be $45 \pm 6\%$, an improvement over the $31 \pm 7\%$ for the nano-SnO_xC_y/PMPDI/CoO_x system.¹⁵ The observed improvement in photocurrent with the addition of catalyst in actual WOC for the ALD-SnO₂ system is, once more, consistent with and supportive of the carbon-impurity hypothesis.

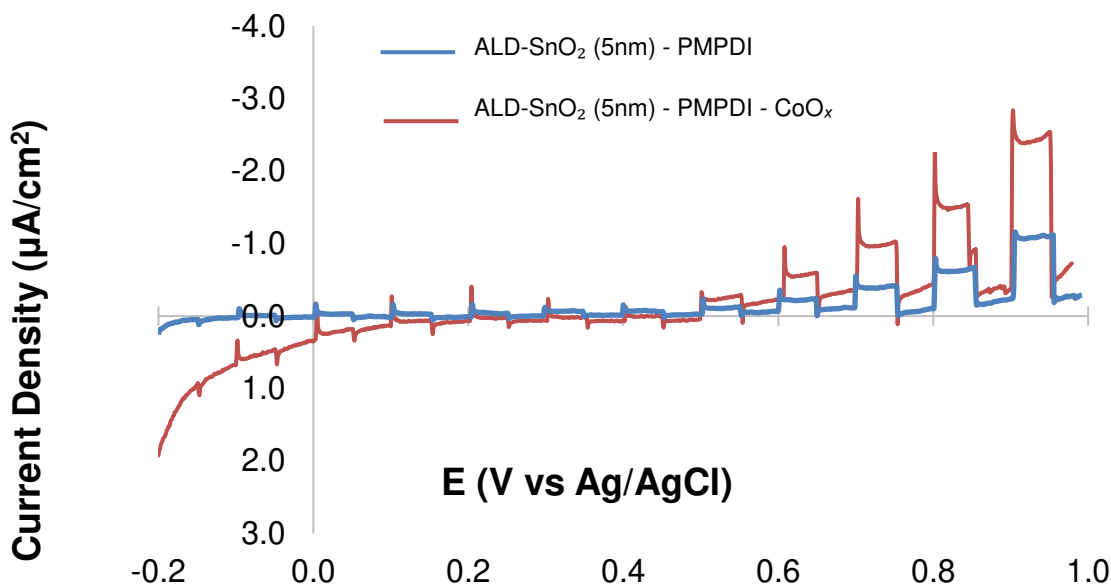


Figure 3.10. Photocurrent transients for ALD-SnO₂(5nm)/PMPDI (blue) and ALD-SnO₂(5nm)/PMPDI/CoO_x (red), anodes. Scans were carried out from -0.2 to +1.0 V versus Ag/AgCl with 5 s light dark transients. Note background currents and current from background FTO subtracted off.

The ALD-SnO₂ systems have a higher (more positive) photocurrent-onset-potential and a larger overpotential is required to see significant amounts of photocurrent. This change in needed overpotential is interesting and implies altered kinetics of charge transfer between the two systems with their differing types of SnO₂ and nanostructured versus planar morphologies. The significant spiking behavior, seen previously and attributed to charge recombination caused by metal-oxide surface states, is still present.^{15,16,57–59}

Perspective and Suggestions for the Field Going Forward

Historically, the impact that carbon-based impurities in metal-oxides have on charge transfer kinetics in DS-PECs is a neglected area of study or, even, recognition. The role of C-based impurities is typically dismissed or at least insufficiently examined. Herein, we have demonstrated

that residual-carbon impurities play a significant part in determining the effectiveness of charge transfer for water oxidation in the system examined, and likely in many other metal-oxide systems that make use of especially polymeric carbon-based stabilizers that are difficult or nearly impossible to subsequently remove completely. Our findings teach that the role of impurities, carbon-based as discussed herein, oxide-based as discussed elsewhere,³² and likely other-element impurities specific to a given system, must be included in the discussion of kinetics and other explanations of the system at hand and its properties.

Additionally, creating at least a working kinetic scheme such as Figure 3.8 is important en route to understanding complex photocatalytic systems, such as WOC systems, and the interconnected pathways that dictate net charge transfer. More specifically, C-based impurities as a now precedented hypothesis for recombination need to be considered in systems with metal-oxide nanoparticles involving polymeric or other hard-to-remove (if not impossible to remove completely) stabilizers. The broader applicability of our results is illustrated by their relevance to a state-of-the art 2020 system³² where oxide impurities are considered, but carbon impurities are noted but not assessed. *Both* carbon impurities and oxide defects need to be addressed in such cases as both can play critical roles in altering the kinetics of charge transfer pathways and, hence, the overall WOC results.

It is important here to note that advanced techniques like ALD that involve much less carbon are certainly more costly and technically involved than the simple doctor blading method used for nano-SnO_xC_y. Such more sophisticated methods are less easily scalable and, hence, may not be sustainable, long-term solutions to depositing metal-oxides with lowered carbon content. As such, our results highlight strongly the need to develop M_xO_y nanoparticle syntheses without the use of polymer stabilizers and, if possible, readily and completely removable *meta*-stabilizers. Indeed,

this need reflects a more general theme and need throughout nanoparticle chemistry, one we have addressed in $M(O)_n$ (M = transition-metal) nanoparticles via the concept of “weakly ligated, labile ligand” nanoparticles.⁶⁰ Such improved syntheses should also strive to be closer to being atom economical²⁴ and to obeying the relevant principles of green chemistry.^{25–27}

Alternative syntheses of pure nano-“ SnO_2 ”, as well as other metal-oxides, that balance minimizing carbon impurity while maximizing surface area are, hence, of considerable interest.⁶¹ Notable here is the Boettcher group’s development of precursor chemistry for the deposition of both undoped and F-doped SnO_2 films using minimal nonfunctional counterions, no organic ligands, and water as a solvent is a promising pathway towards realizing the development of SnO_2 without detrimental carbon states.⁶¹ Perhaps another approach to overcome the recombination kinetics inherent in a material with carbon impurity is the addition of a more efficient catalyst, conceivably one derived from less earth-abundant metals. This approach is under investigation as well.

CONCLUSIONS

Herein, we examined WOC systems consisting of SnO_2 , both nano-“ SnO_2 ” that proved to actually be SnO_xC_y and planar SnO_2 deposited by ALD, coated with PMPDI with a CoO_x catalyst. We were able to answer four important questions: (1) First, is C left as an impurity in nano-“ SnO_2 ”? *Answer: yes.* (2) Second, if so, what then is y in “ SnO_xC_y ”? *Answer: $y = 0.22$.* Third (3) if $y \neq 0$ so that C-impurities are present, then is that C-impurity in turn a source of enhanced recombination in the FTO/nano- SnO_xC_y /PMPDI/ CoO_x system. That is, are C-impurities primarily responsible for the observed “anti-catalyst effect” of added, normally effective CoO_x WOCatalyst?

Answer: yes. (4) Can cleaner ALD deposition of SnO_2 be used to deposit lower-C SnO_2 in a, then, planar SnO_2 -modified version of our WOC system, FTO/ALD- SnO_2 /PMPDI/ CoO_x . If so, does the resulting system exhibit a normal “positive catalyst” effect? *Answer: yes.* Finally, a short section on “Perspective and Suggestions for the Field Going Forward” was provided with the goal of more efficient future research involving M_xO_y nanoparticles in photoelectrochemical devices without the pitfalls that C-based impurities otherwise engender.

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IV. TWO METHODS OF OVERCOMING RESIDUAL CARBON-INDUCED RECOMBINATION IN A WATER-OXIDATION CATALYSIS DEVICE: EMPLOYING AN IMPROVED CATALYST, REDUCING THE RESIDUAL CARBON, AND QUANTITATING THE RESULTANT IMPROVED DEVICE³

OVERVIEW

Previously a dye-sensitized photoelectrochemical cell, composed of nanostructured SnO₂ coated in perylene diimide dye (N,N'-bis(phosphonomethyl)-3,4,9,10-perylenediimide, PMPDI) plus photoelectrochemically deposited cobalt oxide (CoO_x) catalyst, was shown to photoelectrochemically oxidize water. However, the addition of a known water oxidation catalyst, CoO_x, was found to *reduce* photocurrents, the cause of which was discovered to be residual carbon in the nanostructured SnO₂, more accurately represented as SnO_xC_y. Herein we use two different approaches to overcome this “anti-catalyst” effect caused by residual carbon in the nano-SnO₂ structured water-oxidation catalysis (WOC) device. First, we demonstrate the expected photocurrent improvement with the addition of a different, more active, state-of-the-art, amorphous Li-IrO₃-water oxidation catalyst (WOCatalyst). Second, we quantitatively compare, by UV-vis and double layer capacitance, the performance of a more phase-pure atomic layer deposition (ALD) of SnO₂ versus the nano-SnO_xC_y made in house. In comparing photocurrents

³ This chapter details the preparation, characterization, and photoelectrochemical study of a dye-sensitized photoelectrochemical cell with two different catalysts. A version of this manuscript will be submitted for publication in Summer 2022. The Supporting information of this Chapter IV can be found in Appendix III. This chapter was written by the author of this dissertation, C. F. Jewell, with minimal edits and organization suggestions from the author’s advisor. Minor changes were made to meet dissertation formatting guidelines.

based on both a per dye and per electrochemically active surface area basis the more phase-pure ALD-SnO₂ yielded higher photocurrents. Together, these results offer two successful approaches to overcoming and outcompeting recombination attributable to residual carbon in WOC devices.

INTRODUCTION

Rising global demand for renewable energy has led to increased interest in and research on storable solar energy, particularly through the use of photocatalytic conversion of water into oxygen and hydrogen.¹⁻⁴ A dye-sensitized photoelectrolysis cell (DS-PEC) designed to anodically split water generally requires a minimum of three components: a semiconductor used for charge transport, a molecular light absorbing complex such as a dye, and a catalyst facilitating the oxidation of water.^{1,5,6} Organic dyes have drawn particular interest in recent years as light absorbers for solar water splitting as they are relatively cheap, can be made using all earth abundant elements, and are synthetically highly tunable.¹

WOC is a complex kinetics system with many opportunities for recombination. The use of earth-abundant materials in WOC systems is desirable for sustainable, long-term use and, hence, significant work has been done researching WOC systems comprised of fully earth-abundant elements.^{7-9,10} However, prioritizing more plentiful elements over more efficient catalysts often introduces further inefficiencies so that best performing dye-sensitized water oxidation anodes made of all earth-abundant materials are currently seldom reported and those that are still are not competitive with rare-metal-based metal catalysts (Table 4.1).

Many current state-of-the-art catalysts are made of rare metals including ruthenium¹¹⁻¹⁶ and iridium¹⁷⁻²⁴. Recently, an all earth-abundant anode was made in which a Prussian blue analog was

used with a Janus green B dye on rutile TiO₂ resulting in a photocurrent of 50 $\mu\text{A}/\text{cm}^2$ at +0.8 V versus NHE.²⁵ Notably, charge recombination was cited as an issue in this system.²⁵ Dye-sensitized water-oxidizing photoanodes using rare metals as the catalyst are much more common in the literature and achieve much higher photocurrents. Anodes using Ru-based catalysts have achieved photocurrents on the order of 400 $\mu\text{A}/\text{cm}^2$ at +0.4 V versus NHE²⁶ and 300 $\mu\text{A}/\text{cm}^2$ at +0.36 V versus NHE¹⁵. As such, a rare-element based catalyst was chosen for the research herein in order to optimize photocurrents while addressing the questions posed, *vide infra*.

Table 4.1. Relative photocurrents for selected DS-PEC water oxidation systems using both earth abundant and non-earth abundant catalysts.

Paper	Water Oxidation Catalyst	Dye	Scaffolding	Photocurrent	Light Source	All Earth Abundant System?
Finke and coworkers, 2017 ⁸	CoO _x	PMPDI	nano-SnO ₂	20 $\mu\text{A}/\text{cm}^2$ at +0.4 V vs NHE, pH 7	AM1.5 G	Yes
Karadas and coworkers, 2020 ²⁵	Prussian blue analog	Janus green B	Rutile TiO ₂	50 $\mu\text{A}/\text{cm}^2$ at +0.8 V vs NHE, pH 7	100 mW cm^2 , $\lambda > 420 \text{ nm}$	Yes
Meyer and coworkers, 2022 ²⁷	CoF	D- π -A ^a	TiO ₂	120 $\mu\text{A cm}^2$ at +0.6 V vs. NHE), pH 7	100 mW cm^2 , $\lambda > 400 \text{ nm}$	Yes
Meyer and coworkers, 2017 ²⁶	Ru(bda) ^b	D- π -A ^a	TiO ₂ /Al ₂ O ₃ core-shell	400 $\mu\text{A}/\text{cm}^2$ at +0.4 V vs NHE, pH 4.8	100 mW cm^2 , $\lambda > 400 \text{ nm}$	No
Sun and coworkers, 2015 ¹⁵	Ru-pdc ^c	D-A ^d	TiO ₂	300 $\mu\text{A}/\text{cm}^2$ at +0.36 V vs NHE, pH 7	100 mW cm^2 , $\lambda > 400 \text{ nm}$	No
Bignozzi and coworkers, 2015 ¹⁹	IrO ₂	perylene bisimide	WO ₃	70 $\mu\text{A}/\text{cm}^2$ at +0.30 V vs NHE, pH 3	AM 1.5G, $\lambda > 450 \text{ nm}$	No

^adonor- π -acceptor dye ^bRu(bda)-(pyP)₂ (bda is 2,2'-bipyridine-6,6'-dicarboxylate; pyP is (3-(pyridin-4-yloxy)propyl)phosphonic acid) ^cRu-(pdc)(pic)₃ with pyridine-2,6-dicarboxylic acid (pdc) as an anchoring group, pic = 4-picolinef ^d donor-acceptor dye, 4-(diphenylamino)phenyl cyanoacrylic acid

Previously, our group developed a water oxidation system consisting of all earth-abundant materials: nano-SnO_xC_y coated with a perylene diimide dye, N,N'-bis(phosphonomethyl)-3,4,9,10-perylenediimide (PMPDI), and CoO_x as a catalyst.^{8,9} Although the materials aspect of this system is environmentally friendly, the addition of the CoO_x catalyst resulted in a *decrease* in photocurrent and an increase in recombination.^{8,9} We recently determined this “anti-catalyst” behavior is attributable to carbon impurities in the nano-SnO_xC_y.²⁸ The earth-abundant metal, CoO_x, catalyst cannot effectively outcompete recombination in these nano-SnO_xC_y water oxidation catalysis (WOC) anodes.

Herein, we pose the questions (1) “Can improving the WOC catalyst to one that is best in class overcome and outcompete these recombination pathways?” That is to say, can a more active WOCatalyst alter the kinetics of the WOC system and impact the primary charge transfer pathways? This question serves as a means to study and optimize the WOC device as well as a way to understand how best to research WOC materials moving forward. A second question addressed herein is (2) What, then, is the maximum current from such simple devices (i.e., and as a benchmark for future, better, more successful, earth-abundant WOCs?). As a second means of approaching and understanding how best to deal with residual carbon in the nano-SnO_xC_y, we take a closer look at the use of atomic layer deposition (ALD) of planar SnO₂ as a way to produce a positive catalytic effect upon CoO_x addition.²⁸ Herein, we look to compare the performance of the ALD-SnO₂ device to its nano-SnO_xC_y counterpart in order to determine if an improvement in photoactivity is achieved in the planar system. As such, we (3) report on whether a way can be developed to correct for the very different surface areas of the two systems and, if so, (4) which system is most efficient, the FTO/ALD-SnO₂/PMPDI/CoO_x system or the FTO/nano-SnO_xC_y/PMPDI/CoO_x system? This research offers useful insight into both the way in which we test new

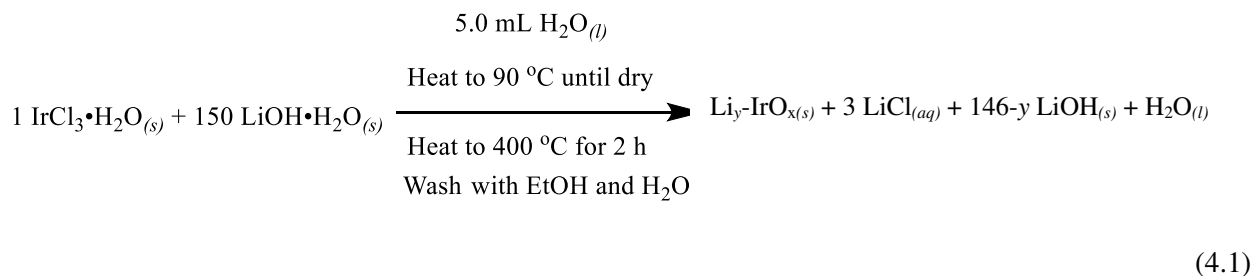
materials for complex WOC anodes to ensure the device components are not limited by catalyst choice as well as a directive to test more earth-abundant catalysts that can effectively compete with the kinetics of recombination.

EXPERIMENTAL

Experimental conditions used herein are identical to those in our previously published work^{7-9,28}, unless otherwise noted. Key experimental details are provided below and in the Supplemental Information as necessary to ensure that the present manuscript is largely self-contained.

Materials. The following starting materials and solvents were used as received to generate buffer solutions: KOH (Fisher, Certified ACS grade, 98.5%, 1.5% water, 0.00028% Fe, 0.0008% Ni); KH₂PO₄ (Fisher, Certified ACS Grade, 99.3%, 0.0005% Fe); Ethanol (Pharmco-Aaper, ACS grade); hydroquinone (Aldrich, >99%); NANOpure water (Barnstead NANOpure ultrapure water system, 18.0 MΩ). NANOpure water was used for all experiments.

Synthesis of Li-IrO_x. To start, Li-IrO_x was synthesized using the Gao²⁹ published synthesizes as written, Eq. 4.1. Briefly, 250 mg of iridium (III) chloride hydrate (Aldrich, reagent grade) was dissolved into 5 mL of water. Then, 5.0 g of LiOH·H₂O (Sigma; 150 equivs versus Ir) was added. This solution was then heated to 90 °C with stirring in order to remove the water by evaporation. The solid remaining was then placed in a crucible and heated to 400 °C for 2 hours under air. After cooling, the resultant solid Li-IrO_x product was rinsed three times each with water and ethanol then dried at 60 °C overnight at 1 atm. The final Li-IrO_x product was found to be comparable to the previously published material by X-ray photoelectron spectroscopy (XPS), detailed in what follows.²⁹



Planar SnO₂ preparation by ALD. As before,²⁸ ultrathin conformal coatings of SnO_x were carried out using the Cambridge Nanotech Savannah S100 ALD system (base pressure of ~ 0.43 Torr) at a temperature of 85 °C. SnO_x depositions were done using sequential exposures to tetrakis(dimethylamido)tin(IV) (TDMASn) (Strem Chemicals) (200 ms) and water vapor (15 ms) with an intermediate purge time of 10 s for both the precursors.

Preparation of nano-SnO_xC_y/PMPDI anodes.

Briefly, nano-SnO_xC_y was prepared as before using a modified literature procedure³⁰ previously optimized for the present system.^{8,28} In short, 800 mg of white commercially available SnO₂ nanopowder (SnO₂, NanoArc® Alpha Aesar, Lot Analysis: 99.6% SnO₂, 47 m²/g specific surface area by BET, 18 nm average particle size, 6.95 g/cm³ density) was massed into a 20 mL scintillation vial to which a Teflon-coated magnetic stir bar was added. The powder was then wetted with 1.0 mL of glacial acetic acid (ACS grade, Mallinckrodt), stirred until fully mixed, and then placed into an ultrasonic water bath (Branson 2510) for 5 minutes. Next, 4.0 mL of water was added to the paste and the resulting mixture was stirred for 5 minutes on a stir plate. The paste was then sonicated twice using a QSonica Q125 ultrasonic liquid microprocessor (1/8" probe), which was held at 80% amplitude. To this mixture, 1.10 g of polyethyleneglycol bisphenol A epichlorohydrin copolymer (PEG-BAE) (Sigma, M_w = 15,000-20,000), which serves as a

thickening agent, was added in individual small chunks while stirring. After all the PEG-BAE had been added and dissolved fully upon visual inspection, one drop (approximately 20 mg) of Triton X-100 (octyl phenoxy polyethoxyethanol, Sigma) was added using a plastic transfer pipet in order to increase adhesion of the paste to the glass substrate. This final paste was then stirred overnight and then refrigerated in a sealed vial. All synthetic and manufacturing details for PMPDI dye can be found in our previous publications.^{7,8} In order to manufacture the nano-SnO₂ anodes, the previously described nano-SnO₂ paste was doctor bladed onto fluorine-doped tin oxide (FTO)-coated glass using a 2-Scotch thickness.⁸ The PMPDI dye was loaded onto the FTO coated in either nano-SnO₂ or ALD-SnO₂ anodes for 24 hours at 95 °C from a saturated solution of fully protonated PMPDI in water.⁸

Deposition of Li-IrO_x onto nano-SnO_xC_y/PMPDI anodes. Li-IrO_x catalyst (2.5 mg) as prepared above was dissolved 1.0 mL of a 95:5 v/v ethanol: water mixture. Previous work using the Li-IrO_x catalyst deposited the Li-IrO_x using a “custom external-mixing two-fluid nozzle”.²⁴ In lieu of this unavailable custom device, a handheld nebulizer (Hudson RCI, Micro Mist) was used with air to spray droplets of the Li-IrO_x solution onto the anode. Air pressure was set to the minimum value sufficient to nebulize the solution. Care was taken to ensure the mixture deposited uniformly onto the anode by using a modified nebulizer to narrow the size of the spray to equal the anode size. Further information on the nebulizing device can be found in Supporting Information S2. The resulting anode was then annealed at 120 °C for 10 minutes under air.

Deposition of CoO_x. CoO_x WOC was added to photoanodes by photoelectrochemical deposition.^{7,8} The FTO/SnO₂/PMPDI anodes were placed into a solution of pH 7, 0.5 mM Co(NO₃)₂ and 0.1 M potassium phosphate buffer (KPi) and held at +0.2 V versus Ag/AgCl under 1 sun illumination for 3 min.⁸ Anodes were then rinsed with water for 30 s and allowed to air dry.

Photoelectrochemical testing. All photoelectrochemical experiments were done in a previously described⁷⁻⁹ custom two-compartment Pyrex cell. The custom cell has two compartments separated by a medium porosity glass frit: a working compartment ($1 \times 1.5 \times 1.5 \text{ cm}^3$, 5 mL) and an auxiliary compartment. A CH Instruments CHI-750D bipotentiostat, a Pt wire counter electrode, and a Ag/AgCl (3 M NaCl, +0.215 V versus normal hydrogen electrode (NHE)) reference electrode were used for all experiments. The counter electrode was placed alone in the auxiliary compartment to separate the products from the working and counter electrodes. The reference electrode was positioned in the working compartment near the working electrode anode's surface in order to minimize resistance. The anode of interest was held with an alligator clip to the front wall of the working compartment with the undyed, nonconductive glass side pressed flat against the compartment wall nearest the incoming light. Both sides of the cell were filled with ca. 5 ml of electrolyte (pH 7, 0.1 M KPi buffer), an amount sufficient to cover the dyed film. The anode was illuminated from using a 65 W xenon arc lamp (PTO model A1010), powered using an OLIS XL150 adjustable power supply. The light from the xenon arc lamp was passed through both a bandpass filter (315 – 710 nm, Thorlabs KG3, FGS900S) and an ultraviolet filter (400 nm long-pass, Thorlabs FGL400S) before reaching the anode. The power density of the light was adjusted to match the visible region of the airmass 1.5 global (AM 1.5G) spectrum.⁸ In experiments with transients (interrupted illumination) a manual shutter was used to block the light.⁸ Each anode was tested with a series of electrochemical experiments in the order detailed below: (1) The cell was allowed to short-circuit in the dark for 60 s to depopulate the electrons from SnO₂ sub-bandgap states.⁸ (2) The open-circuit potential, V_{oc} , of the anode was measured versus the Ag/AgCl reference electrode for 90 s both in the dark and (3) again under illumination. (4) A photocurrent transient experiment in which the anode was held at +0.2 V versus Ag/AgCl for 300 s with 30 s

light/dark transients throughout was next conducted. (5) The anode was then allowed to short-circuit again in the dark for 60 s, and the V_{oc} in both the dark (6) and light (7) were remeasured for 90 s each. A current-voltage (i - V) photocurrent transient experiment (8) was performed where the voltage was scanned from -0.2 V to +1.0 V versus Ag/AgCl using a 10 mV/s scan rate and 5 s light transients. For each experiment and each set of conditions being tested, every experiment was reproduced a minimum of three times with three separate anodes prepared under identical conditions. All figures and values reported herein are representative examples of the photoactivity of the anode system indicated. Care was taken to ensure that the reported results are reproducible and are not due to a defective anode or otherwise irreproducible sample.

XPS. XPS (X-ray photoelectron spectroscopy) was done in house using a PE-5800 series Multi-Technique ESCA XPS system. An Al K α monochromatic source operating at 350.0 W was used for all XPS experiments. High resolution (HRES) scans were carried out for all elements present (carbon, lithium, oxygen, iridium) in the initial survey scan at a minimum of 3 spots across the sample surface for 30 minutes apiece. To fit the data, CASAXPS software was used to analyze the data. Quantification results for each element were tabulated using an average of each replicate scan. Consistent with both the literature method of XPS fitting and ensuring self-consistency across fits, HRES spectra were calibrated to a 285 eV aliphatic carbon peak.^{31,32} Fits were done using a minimum, Ockham's Razor type approach to ensure the data was not overfit (Figure S4.1).

Oxygen detection. Oxygen yield was measured using the generator–collector (G-C) technique detailed previously.^{8,9,33–35} Photoanodes of interest, “generators”, were placed with conductive sides facing the conductive side of a FTO “collector”.⁸ The “generator” and “collector” were then separated by a Parafilm spacer. The G-C device was placed in the working compartment detailed above, with the generator side flush against the wall of the cell nearest the incoming light. The cell

was filled with approximately 10 mL pH 7, 0.1 M KPi buffer, sufficient to fully cover the dyed portion of the anode, which was degassed with Ar for a minimum of 60 min to remove oxygen. Current was measured at both the “generator” and “collector” electrodes, which were held at +0.2 V and −0.65 V versus Ag/AgCl, respectively. The current was collected for 300 s in the dark to obtain a background, 300 s in the light to generate oxygen, then 300 s in the dark to ensure all oxygen fully diffused between the two electrodes and that all current attributable to oxygen production was collected. Control experiments with FTO/CoO_x anodes were used to determine the collection efficiency of the G-C device⁸ and used to calculate the O₂ yield and Faradaic efficiency of each photoanode.

RESULTS AND DISCUSSIONS

As a test of our first specific question of how a different WOCatalyst can impact the primary charge transfer a known state-of-the-art WOCatalyst, amorphous Li-IrO_x,^{24,29} was added to an otherwise earth-abundant nano-SnO_xC_y/PMPDI dye-sensitized photoelectrolysis cell (DS-PEC). The addition of the Li-IrO_x to our nano-SnO_xC_y allows us to continue to use the increased surface area provided by nanostructuring the device but seeks to overcome the issue of carbon defects.²⁸ As indicated above, we hypothesized that altering the WOCatalyst used in our nano-SnO_xC_y/PMPDI system might be able to outcompete recombination attributed to carbon in the nano-SnO_xC_y, generating an increase in photocurrent.²⁸ To test this hypothesis we employed the current state-of-the-art, best performing WOCatalysts available, amorphous Li-IrO_x.^{24,29} The highest photocurrent observed for the nano-SnO_xC_y/PMPDI/Li-IrO_x anode is to some extent a measurement of the fundamental limit of our relatively simple, organic-dye and otherwise earth-

abundant device, demonstrating the photocurrents one can strive for with future improved, ideally all earth-abundant, catalysts.

Addition of Li-IrO_x WOCatalyst

Li-IrO_x was synthesized as detailed in the Experimental section and deposited onto the nano-SnO_xC_y/PMPDI, resulting in nano-SnO_xC_y/PMPDI/Li-IrO_x anodes. The photoactivity of these anodes was then examined in pH 7 buffer with the addition of hydroquinone (H₂Q). As before,^{7,8} H₂Q was added to the system as a sacrificial reductant as it exhibits kinetically facile, 2e⁻ and 2H⁺, oxidation.^{1,8,16} Photocurrent transients were carried out on the nano-SnO_xC_y/PMPDI anodes with and without Li-IrO_x catalyst in the presence of H₂Q (Figure 4.1). These results were also compared to our previously published nano-SnO_xC_y/PMPDI/CoO_x⁸ to best understand how changing the catalyst impacts photoactivity. It is important to note here that a comparison of the catalysts based on the number of active sites or amount of catalyst deposited would be ideal but is not yet possible as the amount of catalyst deposited, much less the number of active sites, is not known.

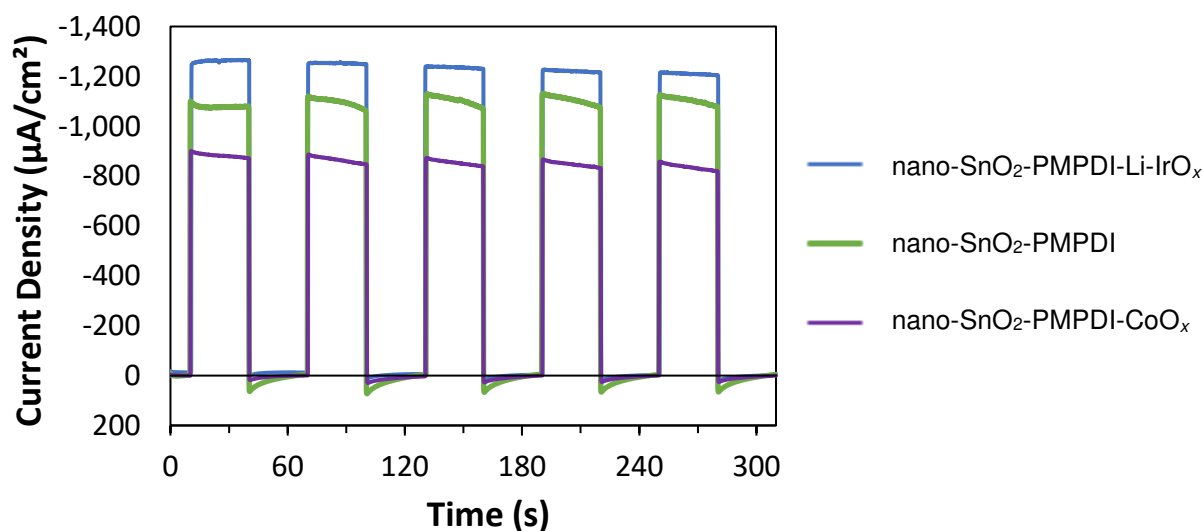


Figure 4.1. Photocurrent transients in the presence of 20 mM H₂Q sacrificial reductant, with background dark current subtracted, at +0.2 V versus Ag/AgCl in pH 7, 0.1 M KPi buffer with 30 s light/dark transients where blue is nano-SnO_xC_y/PMPDI/Li-IrO_x, green is nano-SnO_xC_y/PMPDI, and purple is nano-SnO_xC_y/PMPDI/CoO_x. Note here that each transient shown represents a minimum of three replicates of separately generated and tested anodes.

Importantly, steady-state photocurrents *increase* 10% with the addition of Li-IrO_x, *the first time we have observed an increase in the nano-SnO_xC_y containing anodes.*^{8,9} This increase in photocurrent in a net improvement of 34% from the anode with the CoO_x catalyst to the Li-IrO_x catalyst. As reported previously, anodes with CoO_x WOCatalyst addition yield a *decrease* in steady-state photocurrents of 24% upon catalyst addition.²⁸ By changing the catalyst used with the nano-SnO_xC_y/PMPDI anodes the impact of the catalyst addition is significantly altered; with one catalyst, CoO_x, an anti-catalyst effect is observed and photocurrents decrease but with the addition of the other, rare-element metal-based, catalyst, Li-IrO_x, the photocurrents increase.³⁶ This difference in catalytic impact implies that, not unexpectedly, changing the catalyst alters the kinetics of charge transfer in the anode. However, while the CoO_x catalyst cannot compete with the recombination pathways, the Li-IrO_x catalyst appears to be able to overcome and, at least to some degree, outcompete recombination. Two times the -1.2 mA/cm² photocurrent observed for the nano-SnO_xC_y/PMPDI/Li-IrO_x system in the presence of H₂Q represents the upper limit of the highest fundamental photocurrent for water oxidation using this simple dye-based system. Of note, there is also *significantly less photocurrent decay* over the course of the 30 second light transients for anodes with deposited Li-IrO_x, suggestive of apparent electron-delivery-kinetics protective of the oxidized dye.

To ensure the effect of Li-IrO_x addition in H₂Q was reflective of the true WOC performance, anodes with and without catalyst were examined in pH 7, 0.1 M KPi buffer without any added sacrificial reductant (Figure 4.2). As in the system with H₂Q, the addition of the Li-IrO_x

catalyst to nano-SnO_xC_y/PMPDI anodes again *increases* the system's photocurrent, contrary to what is observed using the nano-SnO_xC_y with CoO_x as the catalyst.^{8,9} With the addition of Li-IrO_x, the steady-state photocurrent of anodes increases by 50%, an increase greater even than seen in anodes tested with the H₂Q. This larger increase in photocurrent with catalyst addition in water is expected because the 2 e⁻ / 2 H⁺ reaction with H₂Q is kinetically much more facile than the more difficult, 4 e⁻ / 4 H⁺, water oxidation reaction of interest. Thus, recombination is likely inherently less for H₂Q versus H₂O due to the inherently higher probability of recombination in the slower, more difficult, overall 4e⁻/4H⁺, water oxidation reaction.

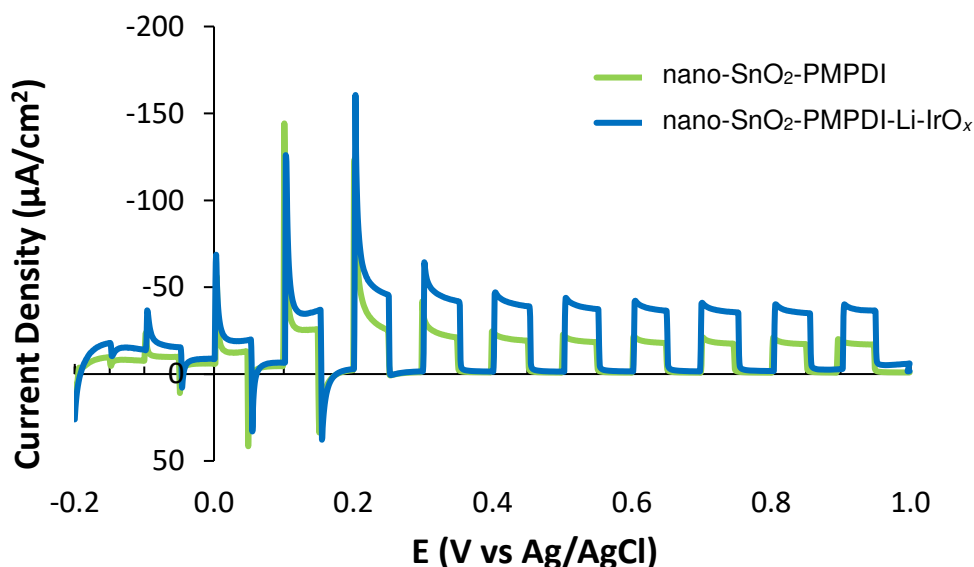


Figure 4.2. Photocurrent transients for nano-SnO_xC_y/PMPDI (green) and nano-SnO_xC_y/PMPDI/Li-IrO_x (blue) anodes in pH 7, 0.1 M KPi buffer. Scans were done from -0.2 to +1.0 V versus Ag/AgCl with 5 second light dark transients.

Understanding Recombination with Different WOCatalysts

To provide more direct evidence that this increase in photocurrent corresponds with a decrease in recombination, the open circuit voltage (V_{oc}) of the anode under illumination was measured.^{8,9,37} In this system, the V_{oc} can be directly related to recombination as the V_{oc} signifies the quasi-Fermi energy of electrons ($E_{F,n}$) in the nano-SnO_xC_y, with respect to the Ag/AgCl reference electrode

potential.^{8,9,37,38} The V_{oc} is determined by the steady-state charge-carrier concentration. This means that the relative rates at which electrons are both injected from the photoexcited PMDPI to SnO_2 and depopulated from the SnO_2 via recombination determines the equilibrium. Thus, the V_{oc} values of nano- SnO_xC_y /PMPDI anodes without catalyst, with CoO_x added, and with Li-IrO_x added were compared to understand the changes in recombination (Figure 4.3).

Notably, we found an average of -0.07 ± 0.03 V versus Ag/AgCl V_{oc} for nano- SnO_xC_y /PMPDI/ Li-IrO_x anodes, a measurable improvement over the 0.00 ± 0.02 V versus Ag/AgCl V_{oc} for anodes without the catalyst.⁸ The -70 ± 30 mV shift in V_{oc} of nano- SnO_xC_y /PMPDI/ Li-IrO_x anodes relative to nano- SnO_xC_y /PMPDI anodes suggests a ca. 15-fold decrease in the rates of recombination relative to injection^{8,37} for the system without the Li-IrO_x catalyst. For comparison, the addition of CoO_x catalyst yields a V_{oc} of 0.05 ± 0.02 V versus Ag/AgCl ,⁸ consistent with an increase in recombination in the CoO_x catalyst system.

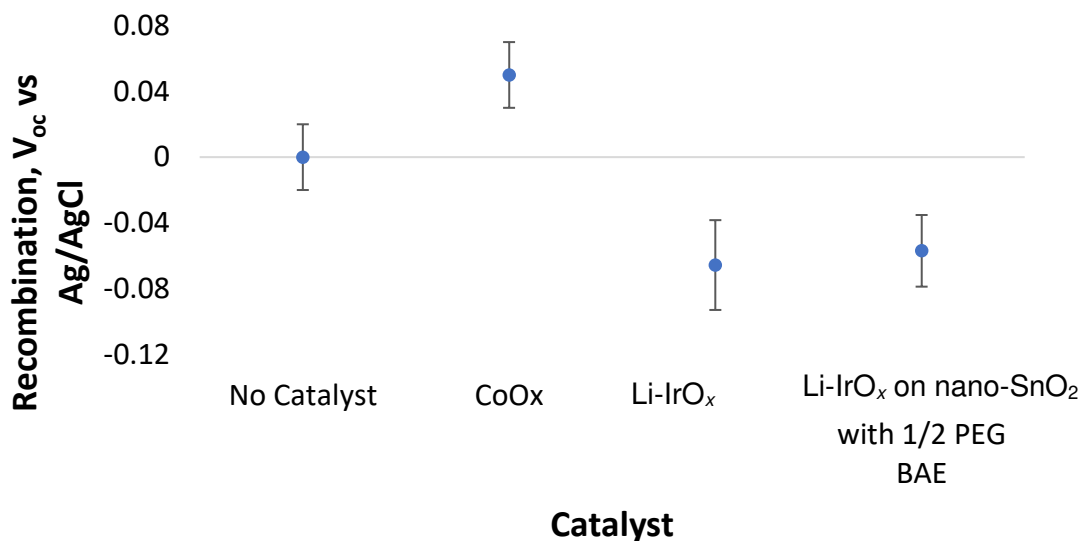


Figure 4.3. V_{oc} versus Ag/AgCl reference electrode in a half-cell setup for nano- SnO_xC_y /PMPDI anodes with differing catalyst addition. Note, no catalyst is added to the far left data point. In this system, $V_{oc} \approx E_{F,n}$, the quasi-Fermi energy of electrons in the SnO_2 sub-bandgap states.^{8,9}

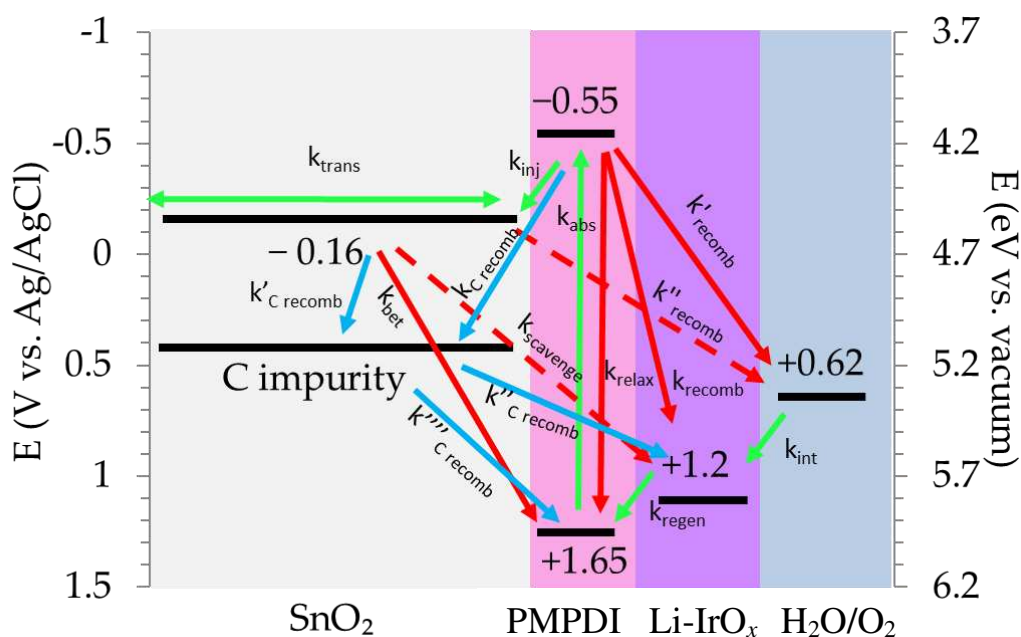
Faradaic Efficiencies for WOC

Often, photocurrent densities in DS-PECs are assumed to be entirely attributable to water oxidation catalysis. As a test of this hypothesis in our device, Faradaic efficiencies for water oxidation catalysis of nano-SnO_xC_y/PMPDI/Li-IrO_x anodes were measured using the generator-collector method.^{8,35} Faradaic efficiencies with Li-IrO_x were found to be $37 \pm 10\%$, the same within error as the $31 \pm 7\%$ for anodes with CoO_x.⁸ The rest of the photocurrent may be attributable to the oxidation of water to H₂O₂, or, less likely to make up the bulk of the photocurrent, the oxidation of trace impurities or degradative oxidation of PMPDI.⁸ Interestingly, the selectivity for WOC of the two devices does not appear to be improved using the Li-IrO_x WOCatalyst in this device. Regardless, the increased photocurrents observed in anodes using Li-IrO_x rather than CoO_x as the catalysts yields an increased amount of oxygen production.

Testing Effect of C-based Recombination

Additionally, anodes were made using nano-SnO_xC_y containing half as much PEG-BAE organic stabilizer, as we have demonstrated previously, to test if Li-IrO_x were seen to fully overcome the carbon trap states. Recombination was found to be the same within error -0.05 ± 0.02 V versus Ag/AgCl and -0.07 ± 0.03 V versus Ag/AgCl for anodes with half as much carbon in the nano-SnO_xC_y and anodes made using the original synthesis, respectively. These recombination values suggest that the Li-IrO_x is able to outcompete and overcome the recombination introduced into anodes by the residual carbon in the nano-SnO_xC_y. Our previous work performing this test to control the amount of residual carbon in anodes using CoO_x resulted in measurable differences in the amount of recombination with respect to the illuminated V_{oc} directly related to the amount of carbon added.²⁸ This provides evidence that a sufficiently effective catalyst can overcome carbon trap states and outcompete recombination pathways,

suggesting that the kinetics of charge transfer in an anode can unsurprisingly be shifted by changing the catalyst.



Kinetics pathways for charge transfer are identified in the scheme using k_{trans} , k_{scavenge} , k_{inj} , k_{recomb} , k_{abs} , k_{bet} , k_{relax} , and k_{regen} indicating, respectively, electron transfer, scavenging, injection, recombination, absorbance, back electron transfer, relaxation, and regeneration. Charge-recombination pathways are shown in red and blue, where blue pathways indicate pathways attributed to carbon defects. Idealized pathways for charge transfer leading to water oxidation catalysis are shown in green. The increased photocurrent and reversal of the “anti-catalyst” effect seen with CoO_x with the use of Li-IrO_x is readily explained by the hypothesis that recombination originating from pathways attributable to carbon is minimized, while more charge transfer occurs through the optimal green pathways with the more active Li-IrO_x catalyst.

However, what is not represented in comparing these kinetic schemes is the changes in the rate constant for each charge transfer pathway that occur by altering the catalyst. We hypothesize, and our data supports, decreased recombination in Li-IrO_x systems, can likely be attributed to increased rate constants for charge transfer in pathways involving Li-IrO_x , specifically k_{int} and k_{regen} . These rate constants reflect charge injection from the WOC reaction into Li-IrO_x and charge regeneration of the dye from Li-IrO_x , respectively. Thus, it is of interest to further investigate in the charge transfer pathways shown in Figure 4.4 by measuring any specific rate constants possible in Figure 4.4 for both the Li-IrO_x , and then also the less efficacious, CoO_x catalyst anodes in the future.

A More Quantitative Comparison of the Planar ALD- SnO_2 versus the Nanostructured SnO_xC_y Systems: Which Is Better?

As a second approach to understand how best to overcome recombination previously attributed to residual carbon in the nano- SnO_xC_y synthesis a comparison of the photoactivity of the more phase-pure ALD- SnO_2 planar system’s performance compared to the nano- SnO_xC_y system was carried out.^{40–44} Previously we observed planar, more carbon-free ALD- SnO_2 could be used instead of nano- SnO_xC_y , which resulted in an expected increase in photocurrent with catalyst addition. However, it is difficult to understand if device performance increases with ALD- SnO_2 versus the nano- SnO_xC_y anodes as the photocurrents of the planar-ALD anodes are significantly

lower. As such, while difficult because of their different (ca. two-order of magnitude, *vide infra*) surface areas, it is of fundamental interest to test quantitatively, if possible, how the ALD-SnO₂ planar system performs compared to the nano-SnO_xC_y system. However, a quantitative comparison between systems of such disparate surface areas, requires a way to correct for the different surface areas, and possibly also any associated differential dye absorption, in the two systems. We employed two methods to compare the two systems based on (i) correcting the data for PMPDI absorbance, or (ii) correcting for the electrochemically-active surface area.

Because of the significantly larger amount of surface area present in the nano-SnO_xC_y system versus the planar ALD-SnO₂ system, significantly different dye absorption is observed. Indeed, saturation-dyeing of the planar and the nanostructured SnO_xC_y systems reveals a stark apparent difference between them (Figure 4.5). In the first method which corrects for the dye absorbance, Beer's Law was employed to calculate the ratio of dye on the planar ALD-SnO₂/PMPDI anode versus the nanostructured nano-SnO_xC_y/PMPDI anode. As before, an approximately monolayer of dye was assumed^{8,45} so as to obtain the PMPDI dye extinction coefficient used in the calculations. Using that extinction coefficient and Beer's law on the UV-Vis data, the ratio of dye absorbance at λ_{max} , after correction for SnO₂ absorbance, was found to be 1:94 for ALD-SnO₂/PMPDI: nano-SnO_xC_y/PMPDI. Additional calculations determining the number of PMPDI dye molecules on both nano-SnO_xC_y/PMPDI and ALD-SnO₂/PMPDI anodes can be found in Appendix III.

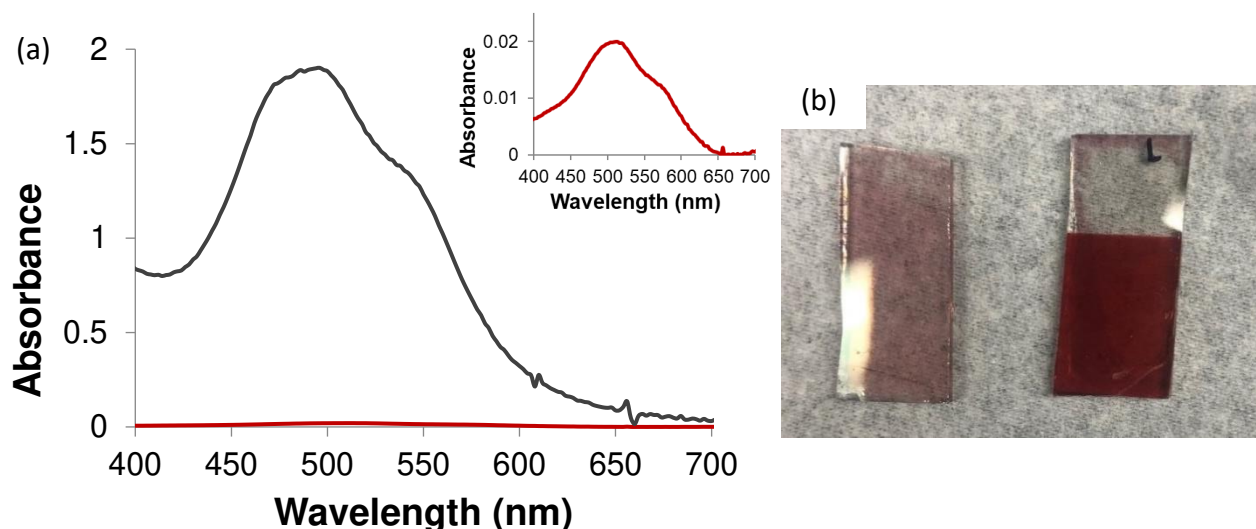


Figure 4.5. (a) UV-vis absorbance spectrum of PMPDI on SnO_xC_y (black) and PMPDI on ALD- SnO_2 (red). Absorbance of bare SnO_2 film was subtracted off. The insert shows a zoomed in plot of the absorbance of PMPDI on ALD- SnO_2 . (b) Image of ALD- SnO_2 /PMPDI anode (left) and nano- SnO_xC_y /PMPDI anode (right), where only the bottom two thirds of the anode is dyed.

Double-layer capacitance (C_d) was employed as a second means to compare and differentiate the electrochemically active surface area between the two systems. By looking at the double-layer capacitance at a series of scan rates a $\mu\text{F}/\text{cm}^2$ scalar could be determined (Figure 4.6 and Appendix III for further details). This scalar was then used with the C_d of the nano- SnO_xC_y system to find the difference between the geometric and electrochemically-active surface area. This value can then be used with the geometric surface area of the nano- SnO_xC_y anode tested to find the electrochemically-active surface area. This method assumes the double-layer capacitance response is the same for the nano- SnO_xC_y and ALD- SnO_2 . Using this determination, the ratio of electrochemically-active surface area for ALD- SnO_2 anodes versus nano- SnO_xC_y anodes was found to be 1:187.

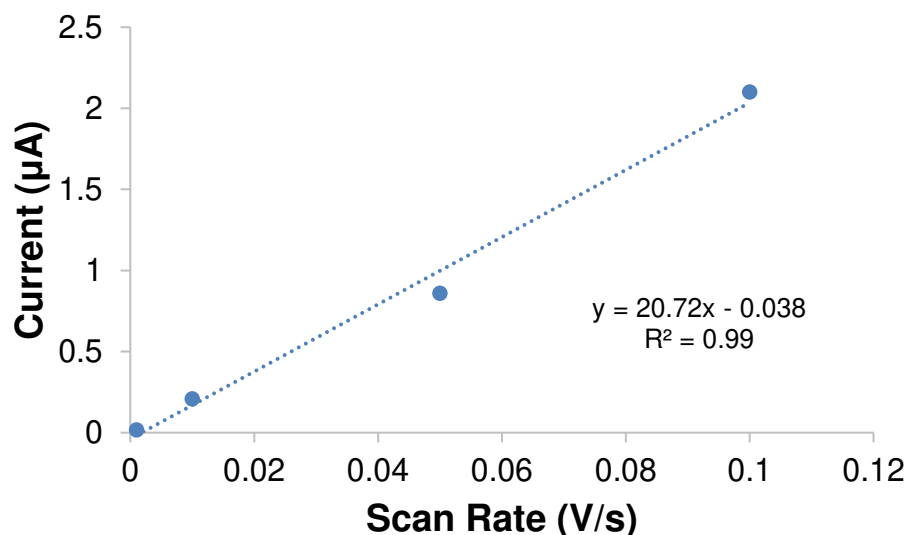


Figure 4.6. Plot of scan rate versus capacitive current for the ALD-SnO₂, where the slope of the line is directly proportional to the double layer capacitance.

The seemingly different 1:94 and 1:187 values are surprisingly close considering how each method measures a separate component of the system. The absorbance method looks at the PMPDI dye on dry anodes, while the capacitance method probes undyed anodes (i.e., prior to dyeing) in solution and while undergoing electrochemistry. Given that the two techniques are measuring different aspects of the systems under two distinct sets of conditions, the factor of two between the values is, again, surprisingly consistent and arguably more than sufficient for the purposes of the present study. So as to not overcorrect and not artificially over-enhance the current (J) data for the ALD-SnO₂ anodes, the corrections that follow will emphasize the smaller, 1:94, value, with, as a control calculation, corrections done with the 1:187 value cited and provided in Appendix III.

To compare the different anodes, the above correction was made on photocurrent transient plots with the addition of H₂Q (Figure 4.7). (The same data corrected using the higher electrochemically-active surface area value is provided as Figure S4.2 of the Supporting Information.) A couple of observations are readily apparent from examining Figure 4.7: first, the

corrected ALD-SnO₂/PMPDI/CoO_x anodes (green trace, Figure 4.7) demonstrate the highest photocurrent, density production of all the systems—a conclusion even more exaggerated if the larger 1:187 correction is used instead (Figure S4.2 of the Supporting Information). Second, the nano-SnO_xC_y/PMPDI/CoO_x system is the worst performer (red trace in Figure 4.7); this conclusion, too, still holds with the larger correction (Figure S4.2 of the Supporting Information). Third, the CoO_x-free systems nano-SnO_xC_y/PMPDI and ALD-SnO₂ (5 nm)/PMPDI perform essentially the same within experimental error (purple and blue curves, respectively in Figure 4.7). These results are fully consistent with and supportive of CoO_x yielding enhanced recombination resulting in the observed “anti-catalyst” effect. (This conclusion, too, is unchanged with the higher correction, although with that the lower-C ALD-SnO₂(5 nm)/PMPDI system outperforms the greater C-containing nano-SnO_xC_y/PMPDI system.) In other words, post scaling the ALD-SnO₂ anodes up to assess performance versus the nano-SnO_xC_y system, the key finding is that the planar SnO₂ outperforms the nano-SnO_xC_y in terms of the current density. This important finding shows that more carbon-free ALD-SnO₂ produces anodes that quantitatively outperform their nano-SnO₂ anode counterparts, on both a per dye and an electrochemically-active surface area basis.

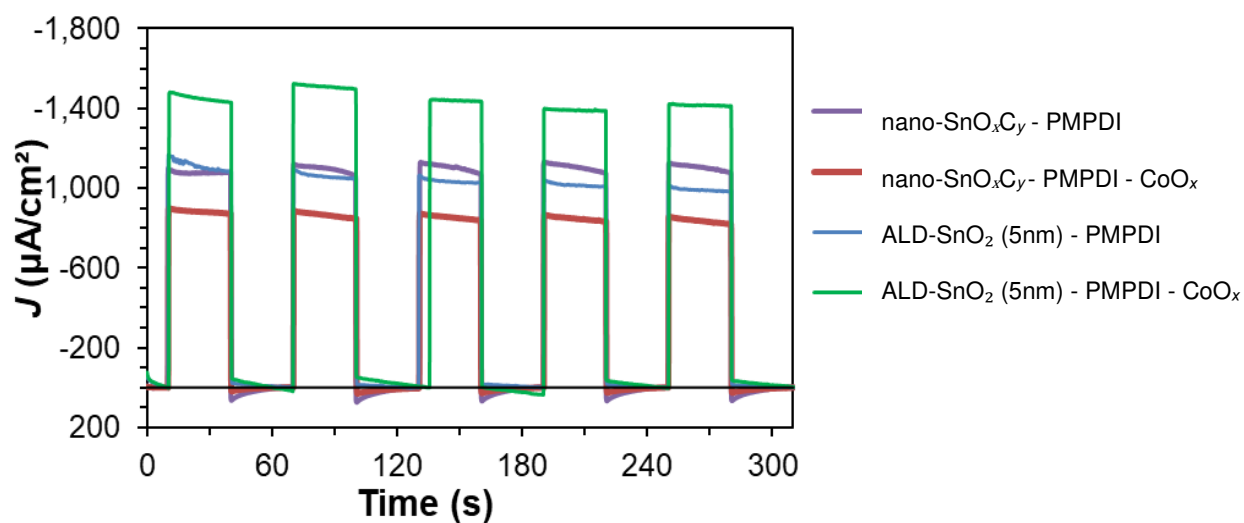


Figure 4.7. J - t transients in the presence of 20 mM H₂Q sacrificial reductant, with background dark current subtracted, at +0.2 V versus Ag/AgCl in pH 7, 0.1 M KPi buffer with 30 s light/dark transients where purple is nano-SnO_xC_y/PMPDI, red is nano-SnO_xC_y/PMPDI/CoO_x, blue is ALD-SnO₂(5 nm)/PMPDI, and green is ALD-SnO₂(5 nm)/PMPDI/CoO_x. Both planar (blue and green) anodes are corrected to match the dye absorbance of the nanostructured anodes.

Perhaps most important are the steady state photocurrents post the addition of CoO_x catalyst: the nano-SnO_xC_y anodes show a *decrease* of ca. 24% in photocurrent while the ALD-SnO₂ anodes show a ca. 44% *increase* in photocurrent. This net 68% reversal of the “anti-catalyst” effect in anodes with less carbon impurity implies that decreasing the amount of carbon by using ALD is a successful strategy to develop more carbon-free anodes and overcome residual-carbon in nano-SnO₂. This strategy is of particular interest as it demonstrates a rare-element-free method of getting around the issue of residual carbon dominated recombination without altering the WOCatalyst. With the ALD-SnO₂(5 nm)/PMPDI/CoO_x anodes, photocurrent densities are comparable to those seen in the nano-SnO_xC_y/PMPDI/Li-IrO_x anodes on a per dye or electrochemically active surface area basis without the use of iridium. If this level of photocurrent density can be achieved using a more carbon-free nano-SnO₂ the use of a rare-element can be avoided while still achieving higher photoactivity. As such, current studies looking into more carbon-free, organic stabilizer-free nano-SnO₂ syntheses are underway.

The photocurrent data in buffered water was then corrected using the previously determined dye absorbance value in order to be comparable to the nano-SnO_xC_y/PMPDI system and was coplotted with the best performing version of a representative anode, nano-SnO_xC_y/PMPDI/PMPDI/AlO_n (0.6 nm, 85 °C deposition) from a previous study⁹ that includes an overlayer of AlO_n deposited by ALD, both with and without CoO_x (Figure 4.8).

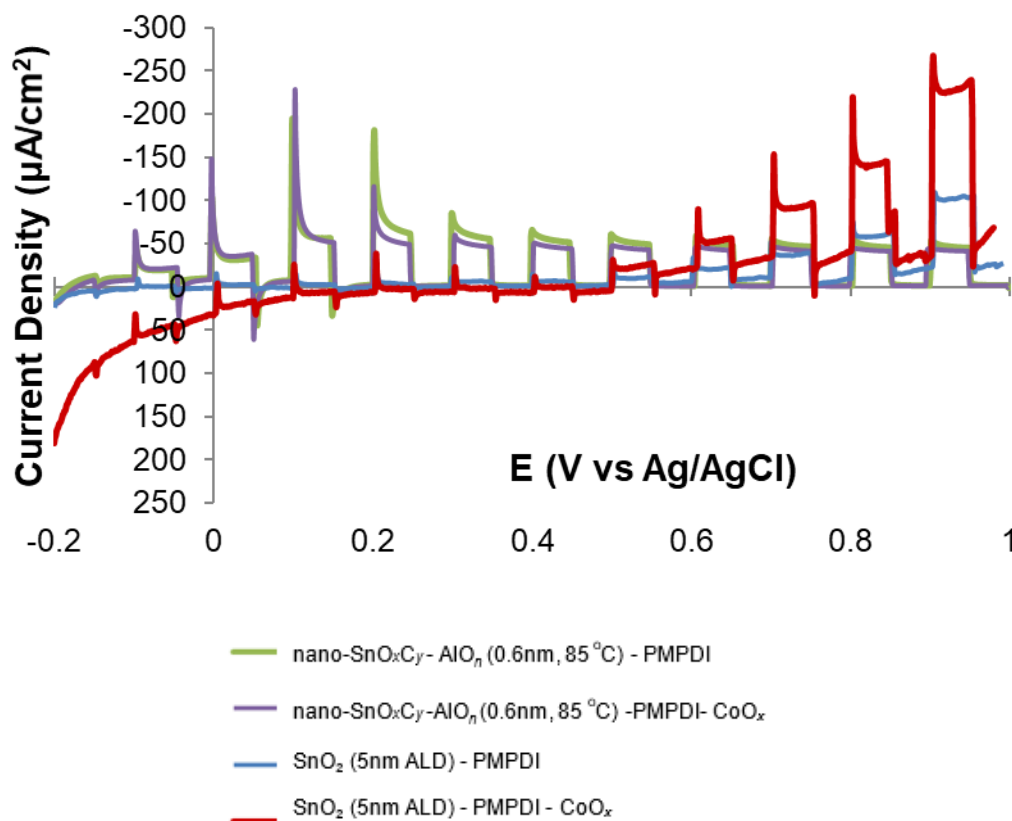


Figure 4.8. Photocurrent transients for ALD-SnO₂(5nm)/PMPDI (blue, corrected for surface area), ALD-SnO₂(5nm)/PMPDI/CoO_x (red, corrected for surface area), nano-SnO_xC_y/PMPDI/AlO_n (0.6nm, 85 °C) (green), and nano-SnO_xC_y/PMPDI/AlO_n (0.6nm, 85 °C)/CoO_x (purple) anodes. Scans were done from -0.2 to +1.0 V versus Ag/AgCl with 5 second light dark transients.

Anodes made using planar SnO₂ deposited by ALD (red and blue traces; corrected for dye absorbance) were shown to have a higher photocurrent than the previous best nano-SnO_xC_y/PMPDI/AlO_n (0.6 nm, 85 °C deposition)⁹ systems (purple and green traces) at potentials over +0.6 V versus Ag/AgCl. It is important to note here that, due to the different thicknesses of the films, diffusion limitations of the H₂Q could be a factor in the comparatively lower photocurrents seen in the nano-SnO_xC_y/PMPDI/AlO_n (0.6 nm, 85 °C deposition) anodes as compared to the ALD-SnO₂ systems.

By quantitatively comparing photocurrents with the addition of catalyst to the planar SnO_2 deposited by ALD to the nano- SnO_xC_y anodes it is clear that using a more phase-pure ALD- SnO_2 is a viable strategy to avoid the residual carbon issue in metal-oxides. We are able to show that the ALD- SnO_2 modified system is an excellent way to mitigate the issue of “anti-catalyst” CoO_x behavior, attributable to residual carbon in metal-oxides. However, it must be noted that while the ALD- SnO_2 system does outperform the nano- SnO_xC_y system on both a per dye and per electrochemically-active surface area basis, the ALD- SnO_2 anodes do have significantly less (ca. 2 orders of magnitude) dye and electrochemically-active surface area. Maintaining the high surface area of the nano- SnO_xC_y systems is of great interest for developing devices with potential future commercial viability. As such, future work looking to build on these findings by designing a more carbon-free nano- SnO_xC_y synthesis that uses both aspects of the work herein, lowering the amount of carbon in the SnO_2 while maintaining the high surface area, is a compelling direction.

CONCLUSIONS

Investigated herein is the impact of changing the water oxidation catalyst on photocurrent, specifically the decrease in current caused by carbon impurity-based recombination in a WOC system. We were able to answer the four specific questions posed at the beginning of the study: (1) yes, improving the WOCatalyst to one that is best in class can change the charge transfer kinetics such that the WOCatalyst can overcome and outcompete recombination pathways. Switching the WOCatalyst from the CoO_x to the state-of-the-art Li-IrO_x resulted in a shift from an unexpected “anticatalytic” decrease in photocurrent with catalyst addition to the expected increase in photocurrent with catalyst addition. The Li-IrO_x was able to outcompete the recombination attribute to a carbon impurities in the nano- SnO_xC_y ,²⁸ where CoO_x cannot. We also found (2) that

the maximum steady state current from such simple organic-dye-based devices, nano-SnO_xC_y/PMPDI/Li-IrO_x, was -42 $\mu\text{A}/\text{cm}^2$ at +0.4 V versus Ag/AgCl in water. Additionally (3), dye adsorption and double-layer capacitance were used as ways to quantitatively compare the two systems. Lastly, (4) *the ALD-SnO₂ modified system* was found to be more efficient than the FTO/nano-SnO_xC_y/PMPDI/CoO_x system.

These results imply that one must look at how each component functions both alone and in conjunction with other materials in the WOC system in order to even begin to understand the kinetics. Without analyzing each component individually and as a whole it is difficult to understand what is limiting the system. If we were to have started with Li-IrO_x as the WOCatalyst initially in 2017, we may never have made our previous discovery about the important role carbon plays in the nano-SnO_xC_y, as the Li-IrO_x would have been able to overcome any recombination introduced by residual carbon. The results presented herein further demonstrate the importance of developing a simple, organic-stabilizer free method of synthesizing nano-SnO₂ with less residual carbon.

Looking forward the results of the work herein suggest several key pathways of research for measurable improvement of DS-PECs. It is also clear that the development of a WOCatalyst that is more selective for water oxidation's 4e⁻ process over the 2e⁻ peroxide reaction is needed. Additionally, kinetic and mechanistic studies looking to verify or refute the proposed Figure 4.4 are needed to rationally move the field forward and achieve true understanding of catalyst performance. It is clear here that more research is needed on all earth-abundant WOCatalysts as well as dye-sensitized WOC systems, both as a means to fully understand each component, but also to understand what and how best to develop and improve these simple but promising devices. Finally, the development of an organic stabilizer-free nano-SnO₂ with less residual carbon is

necessary. Achieving photocurrent densities on the order of the nano-SnO_xC_y system but with the decreased recombination and increased photocurrent densities seen with catalyst addition in the planar ALD-SnO₂ anodes is certainly desirable. DS-PECs are certainly a promising and interesting area of study with many directions of research that are both needed and exciting.

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V. SUMMARY

This dissertation has presented several studies on a dye-sensitized photoelectrochemical cell (DS-PEC) for water oxidation catalysis (WOC). The main project, and the main issue discussed throughout these studies, focuses on the “anti-catalyst” effect of added cobalt oxide water-oxidation catalyst (WOCatalyst) onto nanostructured SnO₂ coated with a perylene diimide dye. A key goal of the thesis is to develop a better understanding of both why this decrease in photocurrent occurs and then how best to overcome it.

Chapter I contained a brief review of solar water splitting, WOC devices, and the current state-of-the-art in the field. The intention of Chapter 1 is to place the work in this dissertation within the perspective of the broader literature, to help the reader understand what devices and systems are of current interest, and ultimately to place the knowledge generated by this dissertation in a broader perspective.

Chapter II described the development of an improved water-oxidizing photoanode consisting of nanostructured SnO₂, coated in a perylene diimide thin film followed by, critically, the addition of an alumina layer (AlO_x) by atomic layer deposition (ALD), plus photoelectrochemically deposited CoO_x WOCatalyst. Throughout Chapter II, 5 key questions pertaining to this device and its photoelectrochemical properties were investigated and answered. It was shown that the deposition of an ultrathin (ca. 1 nm-thick) layer of alumina oxide by atomic layer deposition onto our device results in improvements including decreased charge-carrier recombination and increased steady-state photocurrent densities. Optimizing the alumina overlayer found the best photocurrent densities were achieved using a 0.6 nm thick AlO_x layer deposited at 85 °C on our device. However, the addition of the cobalt oxide catalyst still decreases

photocurrent, even in devices with an alumina overlayer. The study suggests that the alumina layer employed was not thick enough to fully coat the nanostructured SnO_2 , resulting in remaining contact between the CoO_x catalyst and the SnO_2 and, hence, electron / hole trap states. Additionally, a kinetics scheme proposing charge-transfer pathways throughout the device was given. Future studies testing these pathways and measuring the implied rate constants are suggested as a method to achieve better understanding of how and why the alumina-oxide layer improves photocurrent and decreases recombination in this system.

Chapter III presented a study on that same original DS-PEC consisting of nanostructured SnO_2 coated in a perylene diimide with CoO_x as the WOCatalyst with the goal of identifying the source of the “anti-catalyst” effect. Characterization of the nanostructured SnO_2 film by various techniques provided unambiguous evidence for the presence of residual carbon in the films, carbon believed in the literature to be completely removed via annealing. Through careful control experiments and modulation of the amount of organic stabilizer added, it was found that residual carbon impurities from organic stabilizers used in the nanostructured SnO_2 synthesis are to blame. Thus, more chemically accurate description of the nano-“ SnO_2 ” is nano- $\text{SnO}_x\text{C}_{0.22}$. The resulting hypothesis, that carbon impurities are the source of the “anti-catalyst” effect, was then further tested using additions of carbon black, as a known carbon moiety, varying the amount of organic stabilizer added in the initial synthesis, and by using ALD to produce a more carbon-free planar SnO_2 . Additionally, the observed Faradaic efficiencies were found to be $45 \pm 6\%$ for anodes made using ALD- SnO_2 , an improvement over the $31 \pm 7\%$ for the initial nano- $\text{SnO}_x\text{C}_{0.22}$ system.

Proposed future directions for studies resulting from the work in Chapter III include (i) an investigation of other metal-oxides used in the literature made with organic stabilizers to see if the C-impurity problem is as expected a broader phenomenon, (ii) designing syntheses of

nanostructured M_xO_y semiconductors stabilized using a minimum number of presumably non-polymeric, ideally readily removable stabilizing ligands, (iii) a fast spectroscopic kinetics study to measure the relative rate constants and pathways for charge-transfer that involve residual carbon, and (iv) looking to overcome recombination kinetics arising from carbon impurity through the use of a more efficient WOCatalyst.

Finally, Chapter IV described two methods of overcoming the “anti-catalyst” effect and outcompeting the recombination previously found to be attributable to residual carbon in the SnO_2 . First the use of an iridium-based catalyst, amorphous $Li-IrO_x$, instead of the CoO_x otherwise used to date was described. Through the use of $Li-IrO_x$ as a WOCatalyst, the charge transfer kinetics were changed such that the desired positive catalysis effect, rather than the prior “anti-catalyst” effect seen with CoO_x , was observed. This teaches that the choice of water-oxidation catalyst can, as expected, significantly influence the kinetics so that choosing a more effective WOCatalyst can overcome and outcompete recombination pathways.

As a second approach to the “anti-catalyst” issue, planar ALD- SnO_2 anodes with less residual carbon were tested for WOC performance as compared to their nanostructured counterparts using the original CoO_x catalyst. When comparing the ALD- SnO_2 and the nano- SnO_2 anodes on the basis of both electrochemically active surface area and then on the amount of dye adsorption, the ALD- SnO_2 anodes were shown to outperform nanostructures SnO_2 anodes. These results indicate both the need to better characterize and understand the role of each component in a device and as a directive to research both “better” water oxidation catalysts (better able to overcome and outcompete recombination attributed to residual carbon) and also research more carbon-free nanostructured metal-oxides.

Future Direction

There are several additional interesting and promising paths forward for continued research based on the results described in this dissertation. Future work on removing residual carbon from this system and similar systems should start to focus on the synthesis of more carbon-free nano- M_xO_y semiconductors that do not use organic stabilizers. The formation of organic stabilizer free, high surface area, nanostructured metal-oxide films is of great interest as it allows for increased light absorption while maintaining the benefits of a more carbon-free metal-oxide seen using ALD. Research into such organic stabilizer free nanostructured SnO_2 is already underway and will be reported in due course from the Finke group.

One such state-of-the-art nano- SnO_2 synthesis makes use of thermodynamically unstable tin(II) hydroxide nitrate cluster precursors to form 15-25 nm SnO_2 particles.¹ However, this synthesis is extremely complex and somewhat dangerous; hence, finding an alternative synthetic route is recommended. Additionally, films of these SnO_2 nanoparticles were reported to only be 50 nm thick, significantly thinner than the 4 μm (4000 nm) thick films we found to be optimal in our device.^{1,2} Another method that has been used to form nano- SnO_2 without organic stabilizers uses an aqueous citrato peroxo Sn(IV) precursor, forming 20-40 nm particles.³ However, these particles are not well characterized and form very dense layers, which were reported to be a maximum of 320 nm after 20 spin coat and drying cycles, a very lengthy process that still does not achieve a film on the order of magnitude optimal for our device.^{2,3}

Another possible future direction for nano- SnO_2 synthesis could take insight from the synthesis of Co_3O_4 using a simple acetate surface ligand.⁴ Ideally, we hypothesize a simple, carbon-free SnO_2 nanoparticle can be made with NH_4OH and $HOAc$ as a stabilizer at temperatures below 100 °C. Proposed syntheses, following the precedent experimental pathway for Co_3O_4 metal-

oxide nanoparticles, could start with either commercial SnO₂ nanopowder or Sn(OAc)₂. However, assuming these acetate stabilized SnO₂ nanoparticles can be formed, there is some uncertainty as to the ability of these nanoparticles to form a thick enough film for use in a DS-PEC. As a secondary approach to the residual carbon issue one could also attempt to identify a polymer that burns off more completely than the polyethyleneglycol bisphenol A epichlorohydrin copolymer (PEG-BAE) currently used.

Additionally, researchers in this field looking to improve and expand upon the field of DS-PECs would arguably be well-advised to work on standardizing definitions of improvement, increasing reproducibility standards, and on explicit requirements for specific measurements prior to publication. Although some work has already been done on this front,⁵⁻⁷ standardization of practices across the field would help make different researcher's devices much more comparable, allowing for more direct comparisons and more in-depth, arguably better, scientific discussions about different systems. Requirements of Faradaic efficiencies for water oxidation would be a good minimal first step to ensure legitimate discussions of improvement are in fact reflective of water oxidation catalysis performance and not simply measurements of a side reaction or dye or other degradative process.

A separate path forward with this system should certainly involve the study of additional perylene diimide (PDI) derivatives to test the photoelectrochemical properties of these films and their WOC properties. Most importantly, alternative PDI derivatives could and should test the Achilles's Heel of organic-based WOC systems: dye oxidative instability that is one likely limit to device lifetimes. Some specific dyes that have been under discussion in the Finke group for some time are listed in below in Table 5.1 In the PMPDI the N-CH₂ link is likely the most readily oxidizable site, which is a concern particularly under the strong oxidizing conditions for WOC. To

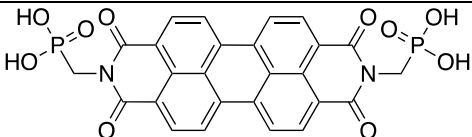
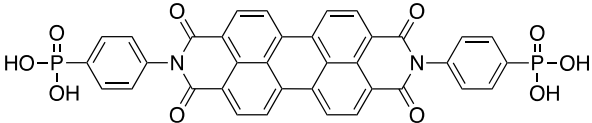
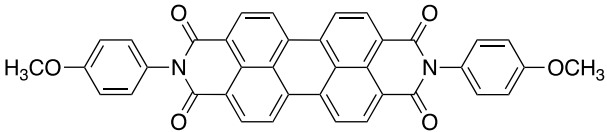
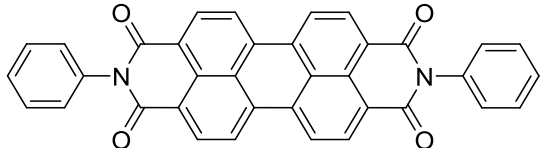
test if this link is the source of dye instability and decreases in photoactivity, PPPDI should be synthesized and tested in a DS-PEC. Understanding dye instability is crucial for the development of future, successful DS-PEC devices.

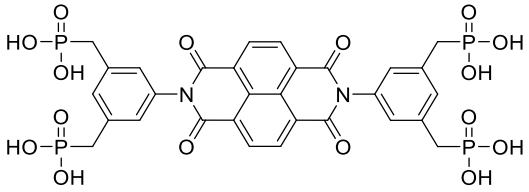
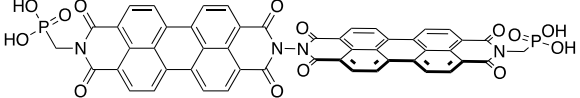
The phosphonate group on the PDI used herein is thought to be important for close electronic coupling between the dye and the inorganic catalyst,⁸ and that can be tested directly via some of the dyes in Table 5.1. MeOPPDI and PPDI, two dyes that do not have the phosphonate linker, can be used as tests of this hypothesis in a DS-PEC. Secondly, a known diphosphonate dye, Phos-NDI, can be tested to see what effect a second phosphate group has on the device's WOC performance.

In addition, a dimeric dye that may promote exciton dissociation and slow down recombination, PMPDI Dimer, is of considerable interest and, hence, merits future studies.

Future studies should also focus on end-of-life studies of DS-PEC devices that look into the anode's failure processes. Analysis of species present in solution may offer insights into either dye or catalyst degradation. Additional investigation into the electrode itself, looking into differences between the anode before and after photochemistry, are another line of inquiry of potential interest. These studies could provide valuable insight into future understanding of instability of DS-PECs. In short, the present dissertation is viewed as a hopefully valuable step in the right direction of DS-PECs and their considerable promise in solar energy conversion and storage for the world's secure energy future.

Table 5.1. PDIs of Interest for Future Testing. For reference, the currently employed PMPDI is shown first, so that it will be clear why the additional PDIs below it are of interest.

Dye Structure	PDI name <i>Abbreviation</i>	References if available	Why this dye is of interest
	N,N'-bis(phosphonomethyl)-3,4,9,10-perylene-3,4,9,10-tetracarboxylic diimide <i>PMPDI</i>	Finke 2014, ⁸ 2017, ² 2021, ⁹ 2022 ¹⁰	Parent dye used in current studies.
	N,N'-bis(4-phosphonophenyl)-3,4,9,10-perylene-3,4,9,10-tetracarboxylic diimide <i>PPPD</i>		This PDI will test if the N-CH ₂ -link in the parent PMPDI, the only obvious more readily oxidizable site in PMPDI, is a cause of loss of photochemical activity / possible dye instability the under strongly oxidizing conditions of photoelectrochemical water-oxidation catalysis.
	N,N'-bis(4-methoxyphenyl)-3,4,9,10-perylene-3,4,9,10-tetracarboxylic diimide <i>MeOPPD</i>	Gravel 1991 ¹¹	This dye will test the need for the -PO(OH) ₂ anchoring group in the parent PMPDI.
	N,N'-bis(phenyl)-3,4,9,10-perylene-3,4,9,10-tetracarboxylic diimide <i>PPDI</i>	Gravel 1991 ¹¹	This dye is a further test of the for the -PO(OH) ₂ anchoring group.

	N,N'-bis(3,5-diphosphonophenyl)-1,3,6,8-naphthalenediimide <i>Phos-NDI</i>	Bhosale 2015¹²	This known diphosphonate dye will test if an additional –PO(OH)₂ group has significant effects on the DS-PEC device.
	<i>PMDPI Dimer</i>		The twisting of the atropisomer twisting of aromatic systems in PMPDI dimer hypothesized to encourage exciton dissociation while also discouraging recombination.

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APPENDIX I: SUPPORTING INFORMATION FOR CHAPTER II

S2.1. Experimental Details for the Atomic Layer Deposition of AlO_x

Ellipsometry Measurement.

To determine the alumina film thickness, the spectral reflectance of Si wafers coated with varying numbers of alumina ALD cycles was measured by a J.A. Woollam M-2000FI ellipsometer. The spectral reflectance data were collected and analyzed using the WVASE32 data acquisition and analysis software (J.A. Woollam Co. Inc.). The incidence angle of the light beam was varied from 50° to 80° with an angle step size of 5° , normal to the substrate plane. The reflectance data were collected over the wavelengths ranging from 200 to 1600 nm. The alumina film thickness was determined by fitting the collected data to a three-layer model ($\text{Al}_2\text{O}_3/\text{native SiO}_2/\text{Si}$) using the known optical constants of the materials available in the software.

Table S2.1: Results of alumina measured by ellipsometry as a function of the number of ALD cycles

Number of ALD cycles	Thickness of AlO_x (nm)
2	0.26
5	0.44
10	0.74
15	1.11
20	1.46

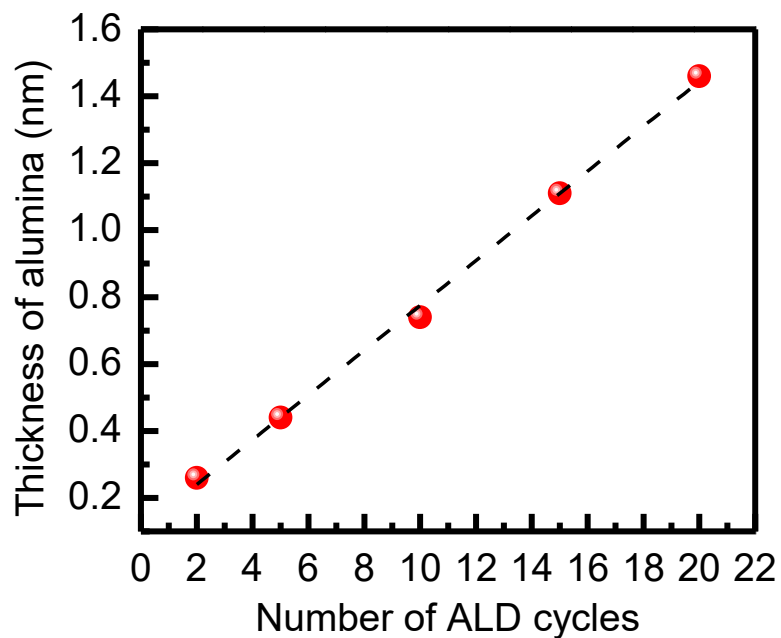
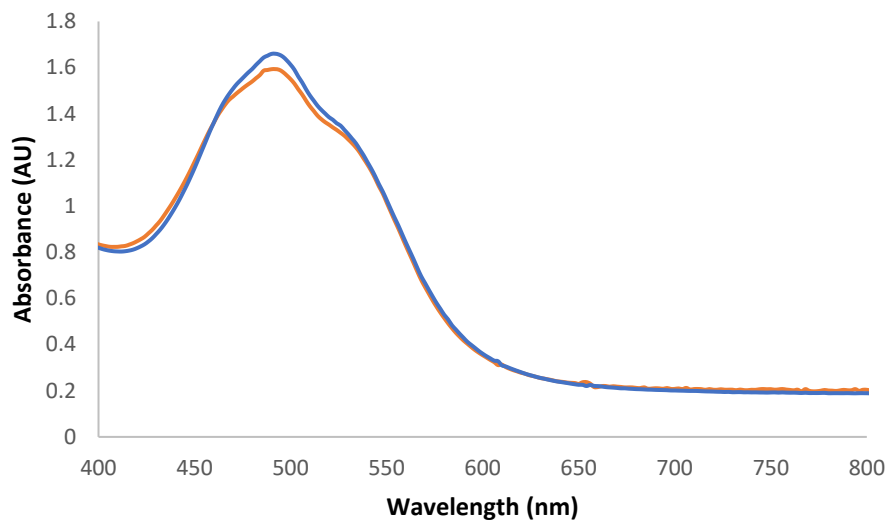


Figure S2.1: Thickness of alumina measured by ellipsometry as a function of the number of ALD cycles

S2.2. UV-vis Spectra of Anodes with and without AlO_x

Using a Hewlett Packard 8452A diode array spectrophotometer, UV-vis data were collected on anodes. Anodes were placed directly against the back wall for consistency and a cleaned FTO slide was used as the reference blank.

a.



b.

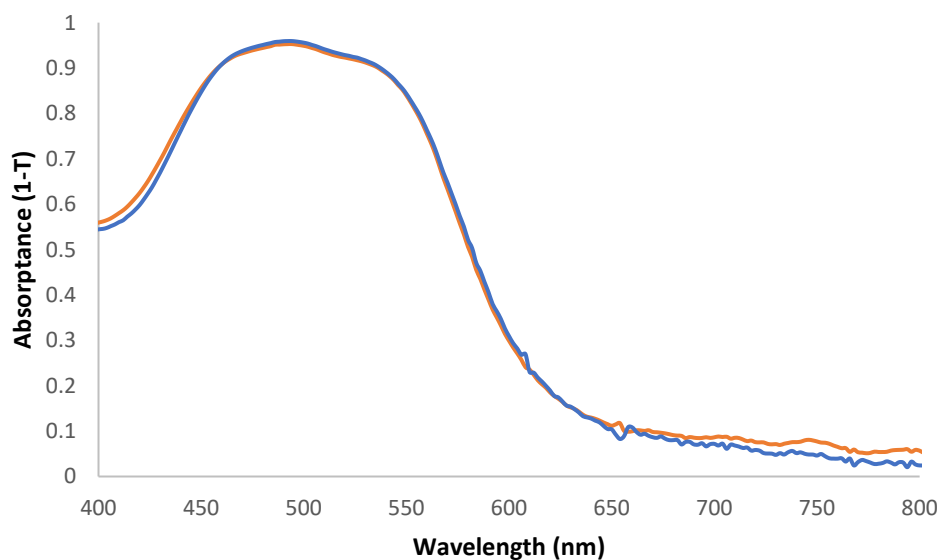


Figure S2.2: Absorbance (a) and absorbance (b) plot for SnO₂/PMPDI (red) and SnO₂/PMPDI/AlO_x (1.3 nm, 85 °C deposition, blue) anodes. Both the degree to which the dye and SnO₂ absorb light as well as the λ_{max} and absorbance pattern remain unchanged after alumina deposition. The UV-Vis of the anode before and after the ALD indicate the bond between the SnO₂ and the dye was unchanged with the addition of AlO_x at elevated temperatures.

S2.3. Photocorrosion Controls on SnO₂/PMPDI/AlO_x/CoO_y

Hydroquinone (H₂Q) was added to the system to examine the anode using a more thermodynamically and kinetically facile reaction. An interesting feature of the photocurrent transient data is the spiking behavior. With the addition of H₂Q, a significant decrease in spiking behavior was observed, and the kinetics of the system appear to be shifted in such a way that the recombination is minimized. Our current leading hypothesis for these large spikes at particularly ca. +0.1 V vs Ag/AgCl are attributable to photocorrosion, but SnO₂ impurities are certainly another hypothesis. Of note, the conduction band edge for SnO₂ is also in the region of high spiking behavior.¹ This may suggest that there is some photocorrosion occurring due to hole accumulation in the system doing water oxidation, but with the easier oxidation reaction, this can be surmounted.

Another interesting feature seen in photocurrent transient plots is an increased steady-state value at +0.1 to +0.2 V vs Ag/AgCl. We currently have not determined the origin of this feature but favor some combination of photocorrosion, degradation, non-water oxidation faradaic processes, or electrochemical processes relating to the SnO₂. We hypothesize that the defects and impurities in our SnO₂ may be related to this feature. As such, SnO₂ by ALD is of great interest to us and future work will explore this hypothesis.

S2.4. AlO_x Photoactivity, Disproof of WOCatalyst Character

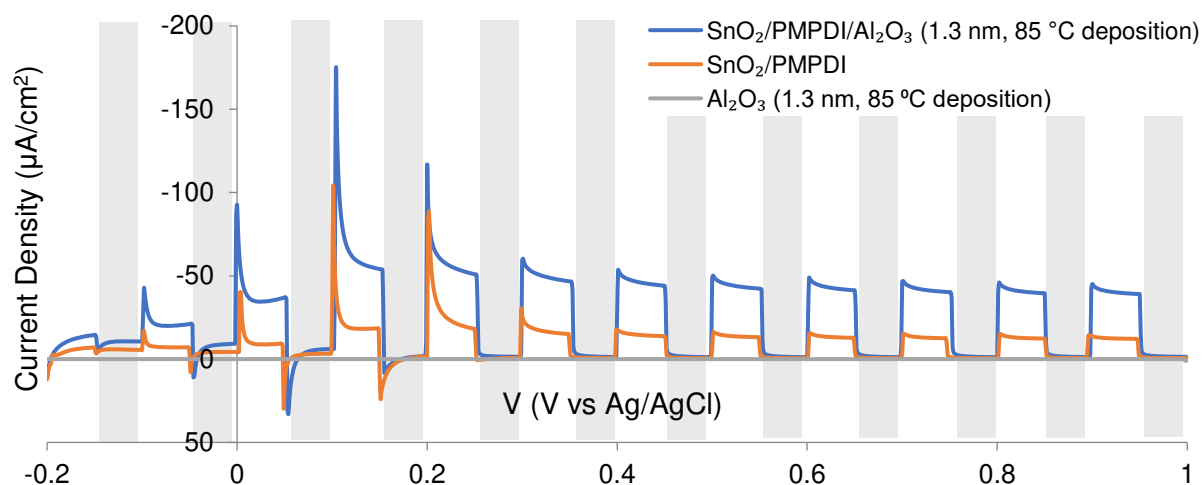


Figure S2.3: Photocurrent transients (with 5 s light/dark transients indicated by white/ gray shading) for $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ anodes (1.3 nm, 85 °C deposition, blue), $\text{SnO}_2/\text{AlO}_x$ (1.3 nm, 85 °C deposition, red), and AlO_x (1.3 nm, 85 °C deposition, green). Scans were done from -0.2 to +1.0 V vs Ag/AgCl with 5 second light, then dark transients. Examining the photocurrents, combined with the negligible oxygen production in the latter two cases, indicates that alumina is not functioning as a WOC.

S2.5. High Resolution XPS of AlO_x

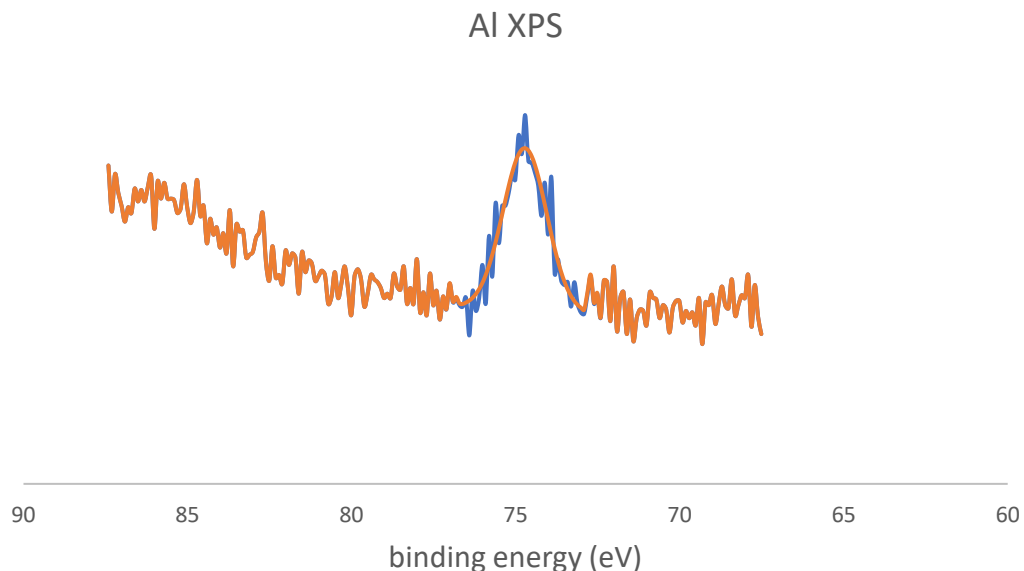


Figure S2.4: Representative high resolution XPS scan Al 2 p electron on alumina as deposited at 85 °C

XPS was carried out inhouse on a PE-5800 series Multi-Technique ESCA XPS system where a Al $K\alpha$ monochromatic source operating at 350.0 W was used for all XPS experiments. High resolution (HRES) scans were carried out at a minimum of 3 spots across the sample surface for 30 minutes apiece. To fit the data, CASAXPS software was used to analyze the data. Consistent with both the literature method of XPS fitting and ensuring self-consistency across fits, HRES spectra were calibrated to a 285 eV aliphatic carbon peak.^{2,3}

XPS was carried out on a sample of AlO_x deposited at 85 °C. XPS detected only one Al environment, corresponding to the oxide (Figure S2.4). O deficiencies, which would appear as a peak at a lower binding energy, can certainly impact the conductivity of the alumina layer. However, in all cases one alumina oxide environment was seen and an O deficiency peak is not present.

Of note, cobalt was not visible by XPS even during extended high-resolution scans due to the very low, catalytic quantities used.

S2.6. Thermogravimetric Analysis of PMPDI Stability

To probe the hypothesis that the PMPDI dye was being degraded under the temperatures used for ALD, a control of thermogravimetric analysis of the dye was done. Though the relatively high thermal stability for an organic compound and dye is one of the primary reasons PDI organic dyes are of interest and used in the present work and other devices, this hypothesis was still investigated. TGA was done using a TA Instruments TGA 2950 Thermogravimetric Analyzer under air flow and using a 20 °C/min heating ramp rate (Figure S2.5). The TGA shows that the dye is stable up to 400 °C, fully consistent with the general literature of PDI dye stability to approximately 300–600 °C.⁴

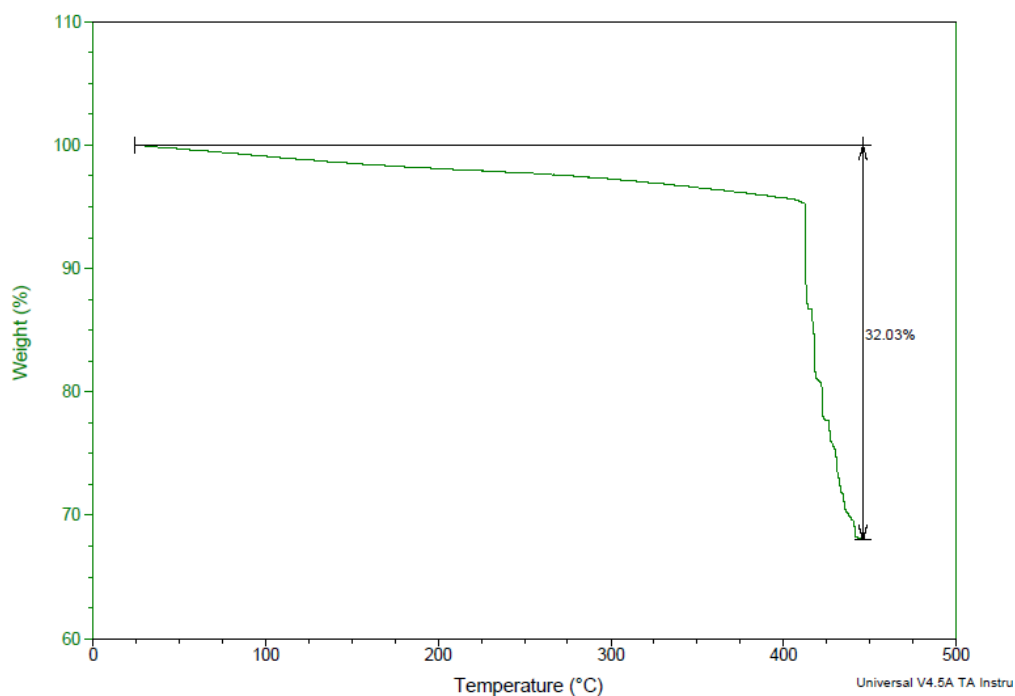


Figure S2.5. TGA of powder PMPDI from 25-450 °C, ramping 20 °C/minute, and under ambient atmosphere conditions. With increasing temperature, there is minimal weight loss up to 400 °C, indicating PMPDI is stable up to 400 °C. This means all AlO_x depositions herein, ranging from 85 °C to 200 °C, do not cause the PMPDI dye to thermally degrade.

S2.7. SEM Image of Anodes

Scanning electron microscopy (SEM) images were taken for $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (0.6 nm, 85 °C deposition) anodes to ensure film morphology remained comparable to previously published SEM images of films without alumina.¹ Images were collected using a JEOL JSM-6500F field emission scanning electron microscope (FESEM), using 15 kV accelerating voltage and 10 mm working distance. Porosity in films was observed.

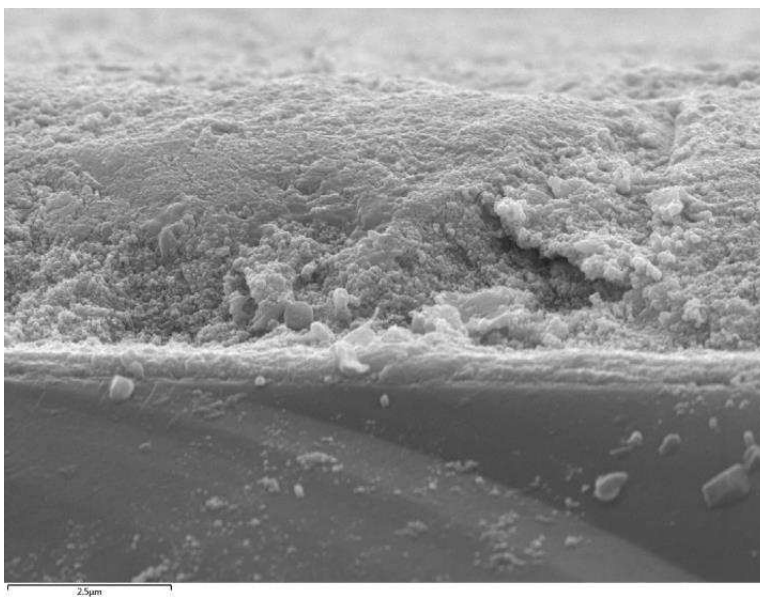


Figure S2.6: SEM image of $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (0.6 nm, 85 °C)/ CoO_y anode taken at 30,000X magnification. Image is a profile of the cross section of the anode after cracking. The FTO glass is clearly visible at the bottom of the SEM image of the cross section for reference and perspective.

SEM-EDS (energy dispersive X-ray spectrometer) data were collected using an Oxford Instruments energy dispersive X-ray spectrometer and Oxford Aztec software was used for qualitative and quantitative elemental analysis. A $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (0.6 nm, 85 °C)/ CoO_y

anode was cracked in half in order to examine the cross section (Figure S2.6). The anode was then coated in 10 nm of gold. The cross section of the anode was then examined using SEM-EDS, though the sample had to be oriented at a slight angle off of vertical, in order to determine if cobalt was seen throughout the sample. Cobalt was not detected due to the very low, catalytic quantity used.

S2.8. Photocurrent Measurement for Optimized Anode for Decay:

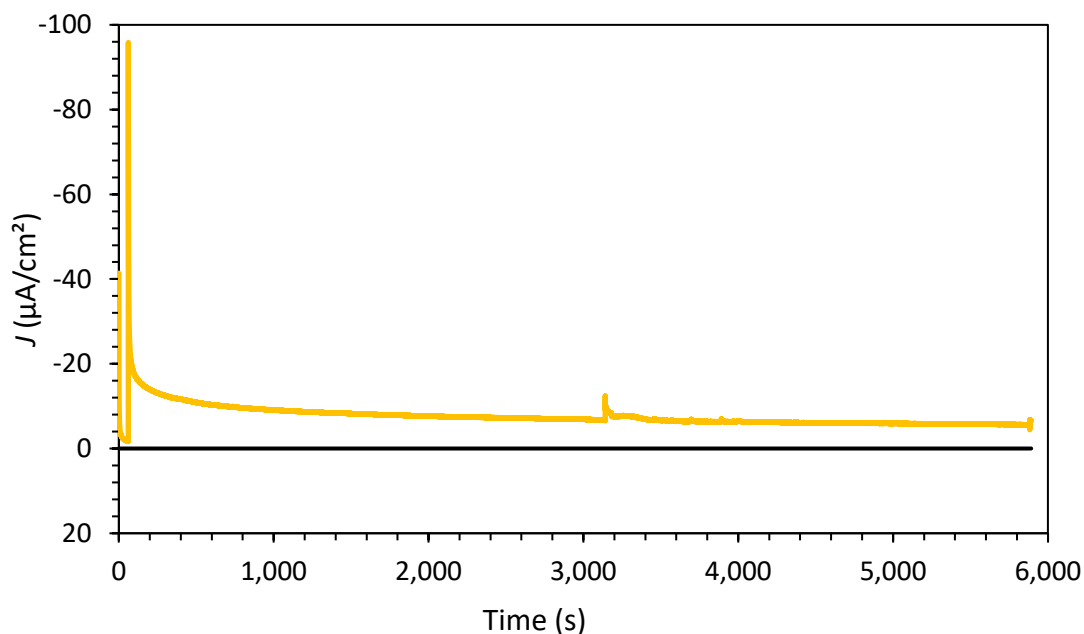


Figure S2.7: i-t of a representative $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x/\text{CoO}_y$ (0.6 nm, 85 °C deposition) anode performed at +0.2 V vs Ag/AgCl in pH 7, 0.1 M KPi buffer. Measurements were taken for over 90 minutes to look at photocurrent decay.

In order to understand the longevity of the photoanode system, the photocurrent density of a representative $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x$ (0.6 nm, 85 °C deposition)/ CoO_y anode was measured at +0.2 V versus Ag/AgCl. In an extended, ca. 1.5 hour long, experiment, a significant, 78%, decay in photocurrent generation was noted. Replicate oxygen detection experiments displayed a decay

in oxygen evolution of approximately 11% after four replicate oxygen detection experiments totaling to 1200 s.

S2.9. Experimental Details for SnO₂/AlO_x/PMPDI System

Deposition of AlO_x was also done on the nano-SnO₂ rather than the SnO₂/PMPDI in order to determine if a more optimal placement of the layer could be achieved. Previously, attempts were made to deposit a near monolayer coating of Al₂O₃ by a solution-based methodology¹, but the observed photocurrents were decreased compared to the system without alumina. Increased dye loading was observed with the addition of the alumina layer in that prior study, although any benefit of increasing the tunneling barrier was counteracted by a reduced injection yield.¹

Herein, once again we observed significantly increased dye deposition kinetics on the SnO₂/AlO_x system. However, the dye deposited onto the SnO₂/AlO_x anodes using the same elevated temperature dying technique discussed in the main text proved extremely unstable physically; any slight movement or agitation in water immediately resulted in the dye flaking off of the anode. Attempts were made to dye the anodes from room temperature solution over a longer period as well as at elevated temperature for a shorter period; however, in every instance the dye immediately fell off the anodes once removed from solution and upon any even very slight agitation.

In future studies, the use of a less aggregated⁵⁻⁹ PDI derivative of the dye could potentially help reduce this preferential binding and stacking of the dye with itself rather than with the SnO₂/AlO_x, resulting in a more viable dye candidate for layering the anodes used herein

with alumina in this position ($\text{SnO}_2/\text{AlO}_x/\text{PMPDI}/\text{CoO}_y$) rather than the $\text{SnO}_2/\text{PMPDI}/\text{AlO}_x/\text{CoO}_y$ architecture used herein.

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APPENDIX II: SUPPORTING INFORMATION FOR CHAPTER III

S3.1. Experimental Details for the *nano-SnO_xC_y* Synthesis

Presented as equation 3.1, the three commercially available precursors, commercial SnO₂ nanopowder (SnO₂, NanoArc© Alpha Aesar, Lot Analysis: 99.6% SnO₂, 47 m²/g specific surface area by BET, 18 nm average particle size, 6.95 g/cm³ density), polyethyleneglycol bisphenol A epichlorohydrin copolymer (PEG-BAE) (Sigma, M_w = 15,000-20,000), and Triton X-100 (octyl phenoxy polyethoxyethanol, Sigma), are combined as described in the experimental forming *nano-SnO₂*. Note that two of the three precursors are carbon-based materials.

In order to balance and write eq (3.1), the synthesis of *nano-SnO₂*, several assumptions were made. First, PEG-BAE has a molecular weight of 15,000 - 20,000. We assumed an average molecular weight of 17,500 in any needed calculations. Then, moles of carbon added were calculated for each carbon containing precursor. Based on TGA data, we assumed 3 wt. % of carbon remained from the initial 1.10 g of PEG-BAE added, (if the same 3 wt. % carbon remains from Triton X-100, the amount of carbon contributed by Triton X-100 is very small and is not statistically relevant). Additionally, acetic acid boils at 118 °C, meaning there is likely little to no carbon incorporation from carbon originating from acetic acid. We therefore assume that all carbon incorporation can be attributed to carbon from PEG-BAE. If there is 3 wt. % PEG-BAE remaining, that value corresponds to 0.0012 moles of carbon for 0.0053 moles of SnO₂, a mole ratio of ca. 1:4.4 carbon to Sn. With such a non-zero molar ratio of incorporated carbon to Sn, there is ample opportunity for the formation of carbon-based trap sites. To simplify eq (3.1), we set the moles of

SnO₂ to be 1, resulting in eq (3.2) in the main text. Eq (3.2) in the main text highlights the 10:1 SnO₂ to carbon addition in our synthesis.

S3.2. Experimental Details for the Atomic Layer Deposition of SnO₂

Table S3.1. Ellipsometry measurements of SnO₂ by ALD

Number of ALD Cycles	SnO _x Thickness (nm)	Standard Deviation (nm)
5	0.50	0.11436
25	2.94	0.14849
50	7.35	0.12021
75	11.06	0.29698
100	14.45	0.49497

To determine the SnO_x film thickness, the spectral reflectance of coated Si wafers was measured over the bandwidth 210–1692 nm using a J.A. Woollam M-2000FI ellipsometer. The incidence angle was varied from 50° to 80° normal to the substrate plane, with a step size of 5°. The collected data were analyzed using the WVASE32 data acquisition and analysis software (J.A. Woollam Co. Inc.), and the SnO_x film thickness was determined by fitting to a three-layer model (SnO_x/native SiO₂/Si) using the known optical constants of the materials available in the software.

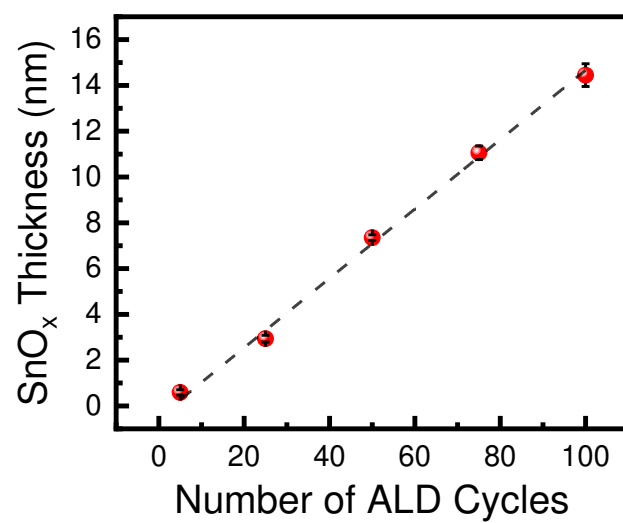


Figure S3.1. Plot of ellipsometry measurements of SnO₂ by ALD

S3.3. Characterization of *nano-SnO_xC_y*

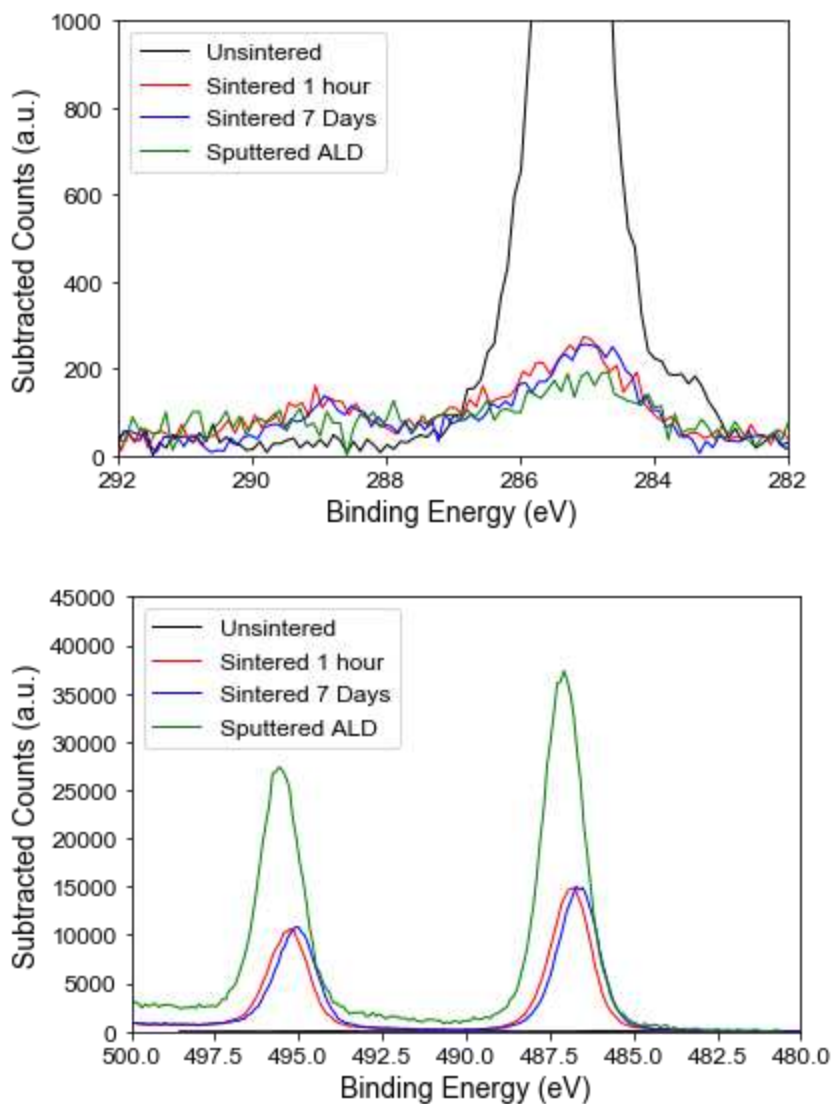


Figure S3.2: Representative high resolution XPS scan of C 1s electron (top) and Sn 3d (right) for ALD-SnO₂ and *nano-SnO_xC_y* anodes under differing degrees of sintering

XPS was carried out on *nano-SnO_xC_y* anodes under differing sintering conditions, from no sintering to sintering for 7 days at 450 °C. Each peak was fit and quantified using a self-consistent fitting method; CasaXPS software was employed to analyze the results. All peaks were fit using the fewest number of fit peaks. Percent chemical concentration of each chemical environment was determined from quantification of the fit peaks and were used to establish the amount of carbon

present in each film. Note here that the data presented above are unfit for simplicity and ease of visual comparison between samples (i.e., an so as to not clutter the figure with fits to the data).

In the case of the unsintered SnO₂ paste, carbon environments were so significant the Sn signal was overshadowed. In the case of the sputtered ALD-SnO₂, the low degree of carbon, which was used as the calibration peak, resulted in a slight shift in the positioning of the Sn peak.

SEM-EDS data were measured for *nano*-SnO_xC_y anodes made with a control 1 equivalent of PEG-BAE used in a typical synthesis as well as with 0.5 and 2 equivalents. To ensure carbon values were representative *nano*-SnO_xC_y anodes, anodes were cracked in half and a cross section of the anode (i.e., looking at the SnO₂ layer from the side such that SnO₂ typically buried was exposed). A minimum of three spots were measured at different depths of the *nano*-SnO_xC_y. SEM-EDS of the *nano*-SnO_xC_y anodes showed the 1 equivalent, typical PEG-BAE addition, to have 10.8 ± 0.8 wt.% C, the 0.5 equivalents PEG-BAE to have 7.8 ± 0.8 wt.%, and the 2 equivalents PEG-BAE anodes to have 26.7 ± 0.7 wt.%. SEM-EDS was also carried out on the ALD-SnO₂ anodes resulting in a 1.68 ± 0.02 wt. % carbon. Representative SEM and EDS can be found both in Chapter III, Figure 3.5, and below, Figure S3.3.

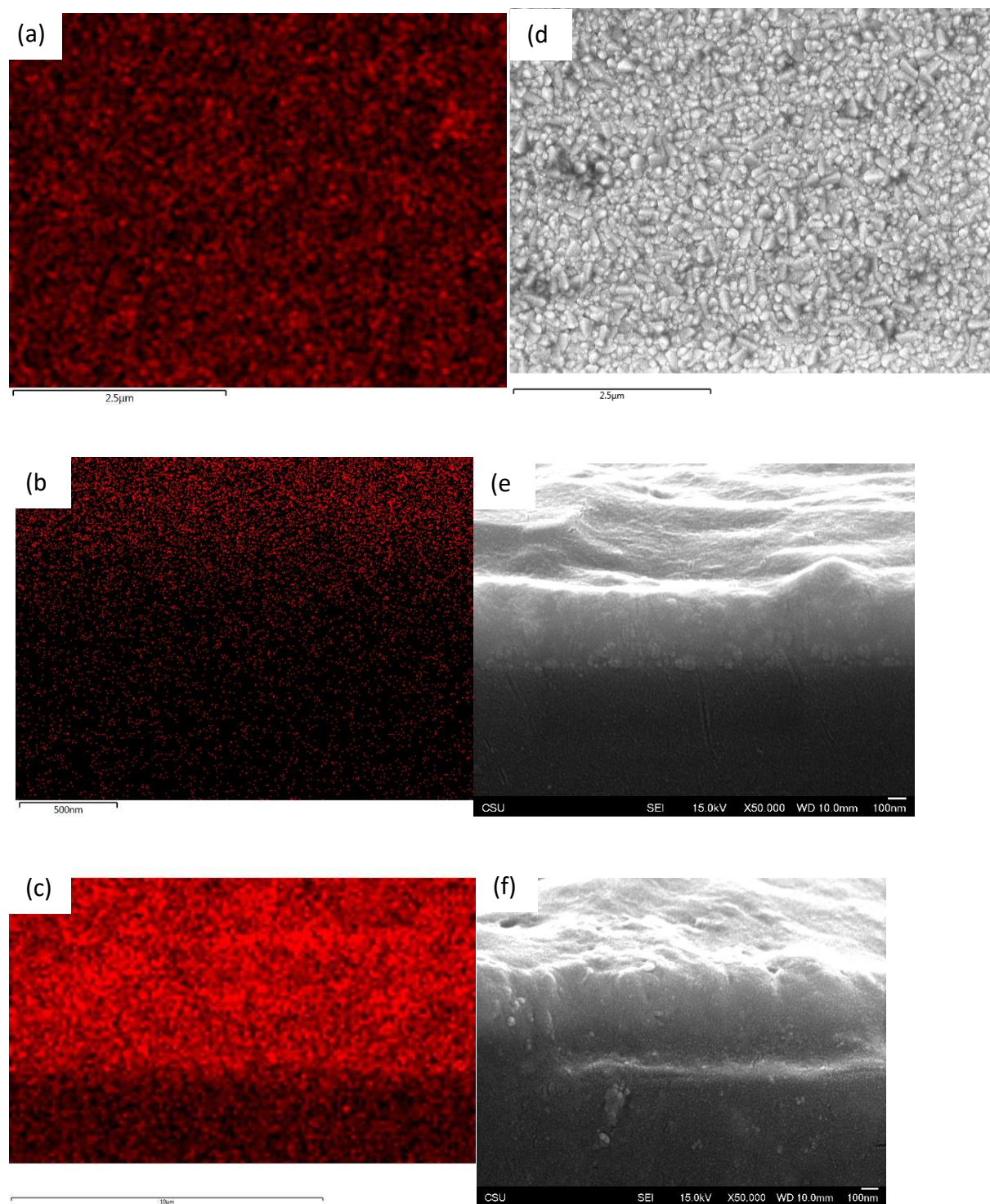


Figure S3.3: Representative carbon EDS of (a) ALD-SnO₂, (b) cracked side profile *nano*-SnO_xC_y 0.5 equivalents, and (c) cracked side profile *nano*-SnO_xC_y 2 equivalents anodes. Both *nano*-SnO_xC_y anodes are shown cracked and the bottom half of each image can be viewed as a background carbon level for comparison. Representative SEM data for (d) ALD-SnO₂ (e) cracked *nano*-SnO_xC_y 0.5 equivalents, and (f) cracked *nano*-SnO_xC_y 2 equivalents anodes.

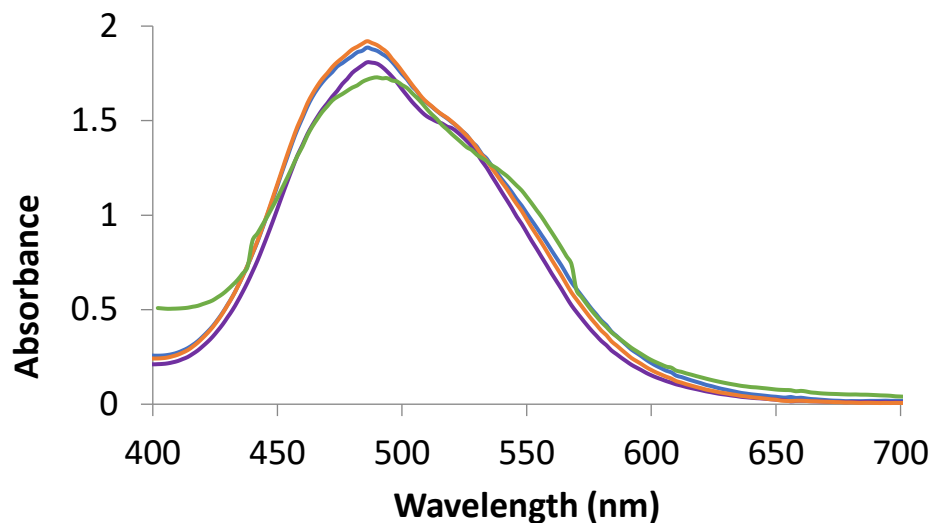


Figure S3.4: Representative UV vis of *nano-SnO_xC_y/ALD-SnO₂* (green), *nano-SnO_xC_y* 0.5 equivalents (purple), *nano-SnO_xC_y* 1 equivalents (orange), and *nano-SnO_xC_y* 2 equivalents (blue) anodes, each coated with PMPDI.

UV-vis was collected for anodes made using *nano-SnO_xC_y/ALD-SnO₂*, *nano-SnO_xC_y* 0.5 equivalents, *nano-SnO_xC_y* 1 equivalents, and *nano-SnO_xC_y* 2 equivalents, each coated with PMPDI, Figure S3.4. This was done to ensure that approximately the same amount of dye was deposited onto films made under each set of conditions. In each case, after subtracting off background undyed SnO₂ films made using the same synthesis as the anode of interest, UV vis analysis indicated the amount of dye was comparable. In all cases, some slight variation in dyeing could be seen across anodes with typical average absorbances at the λ_{max} of 500 ranging from ca. 1.6 – 1.8. The similarity in dye concentration across all synthetic conditions for *nano-SnO_xC_y* and anodes of *nano-SnO_xC_y* coated with ALD-SnO₂ indicates that dye binding affinity is likely not significantly impacted by remaining carbon-impurities under conditions studied herein.

S3.4. Addition of Carbon Black to *nano-SnO_xC_y* paste

Carbon black was added to *nano-SnO_xC_y* in order to further test our carbon impurity hypothesis. To add carbon black to the paste, the previously reported^{1,2} *nano-SnO_xC_y* synthesis conditions used herein were followed. However, prior to heating, additions of carbon black were made to the paste. The paste was then thoroughly mixed for 10 minutes using a clean glass stir rod. The paste was then doctor bladed on to FTO and heated following the conditions detailed in the Experimental Section of the main text. No notable cracking or flaking was observed, but anodes with added carbon black were significantly darker (Figure S3.5).



Figure S3.5. Photo of *nano-SnO_xC_y* anodes without (left) and with (right) carbon black addition. Anodes with added carbon black are notable darker in color and are not translucent.

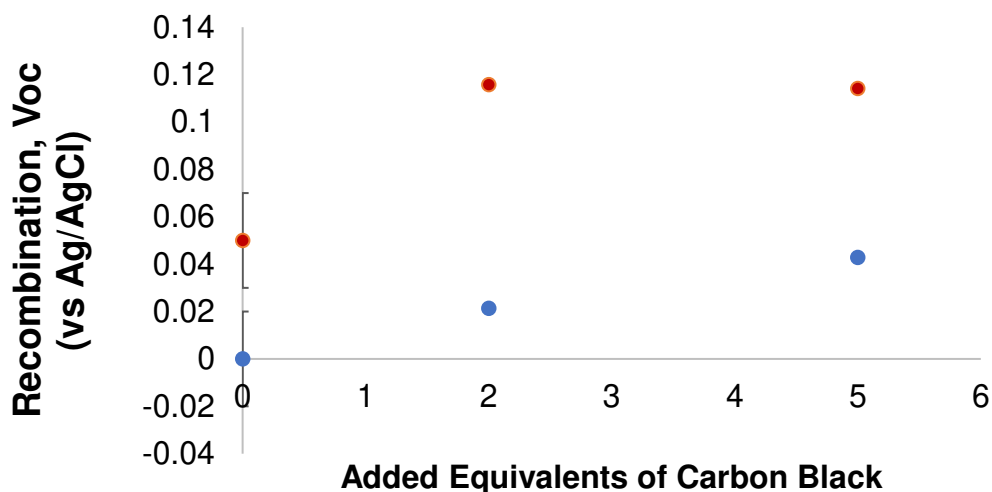


Figure S3.6. V_{oc} vs Ag/AgCl reference electrode in a half-cell setup for *nano*-SnO_xC_y/PMPDI (blue) and *nano*-SnO_xC_y/PMPDI CoO_x (red) anodes at differing amounts of carbon black addition (where 0 added equivalents is the amount added in a typical, traditional synthesis).

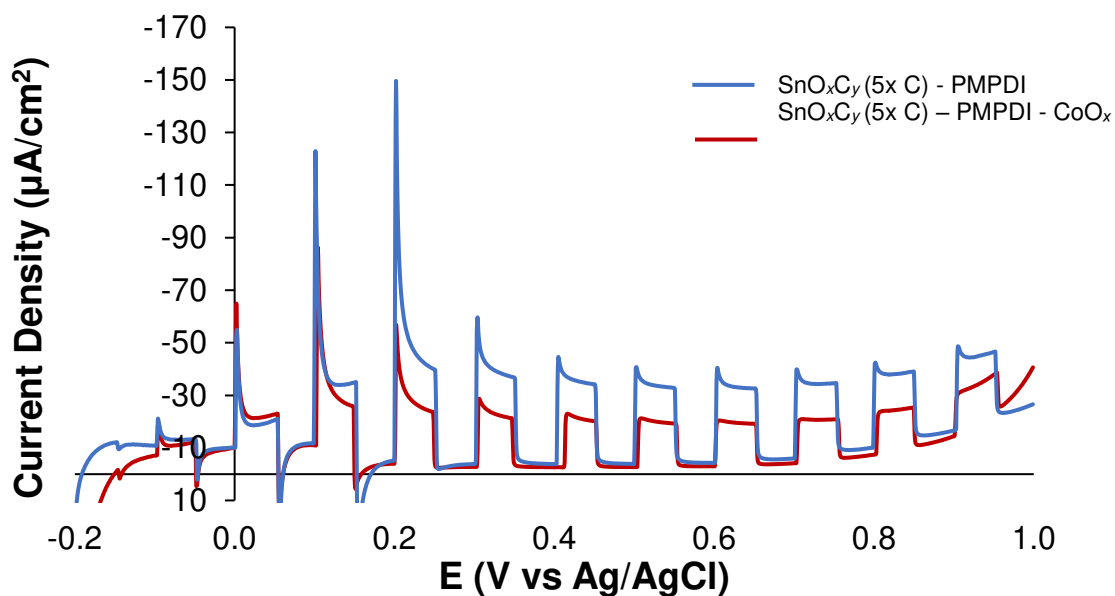


Figure S3.7. Photocurrent transients for a representative *nano*-SnO_xC_y(5x carbon black added)/PMPDI (blue) and *nano*-SnO_xC_y(5x carbon black added)/PMPDI CoO_x (red) anodes. Scans were done from -0.2 to +1.0 V vs Ag/AgCl with 5 second light dark transients.

Recombination was examined in anodes with carbon black at both 2 and 5 equivalents of added carbon black, Figure S3.6. Anodes show a significantly higher level of recombination in

systems both with and without CoO_x compared to anodes without added carbon. For example, increased recombination was observed with the addition of CoO_x in anodes with carbon black added to the *nano*- SnO_xC_y . In anodes with both 2 and 5 equivalents of carbon black a decrease in photocurrent is observed with added CoO_x , Figure S3.7. Overall, the addition of carbon black to the *nano*- SnO_xC_y is consistent with increased recombination pathways as that new source of carbon is introduced, further exacerbating the “anti-catalyst” behavior.^{1,2}

S3.5. *nano*- SnO_xC_y /ALD- SnO_2 /PMPDI

As noted in the main text, in an attempt to find a sort of goldilocks version of the SnO_2 systems in which the increased surface area and dye absorbance of the *nano*- SnO_xC_y and the decreased carbon impurities of the ALD- SnO_2 were balanced, a system combining both forms of SnO_2 was tested. Anodes consisting of *nano*- SnO_xC_y coated in 18 nm of SnO_2 by ALD onto which dye and catalyst were deposited were explored. A thick, 18 nm, layer of SnO_2 was chosen as it was thought to be sufficient to fully coat the *nano*- SnO_xC_y , allowing for a less defective top surface but without the loss of surface area provided by the *nano*- SnO_xC_y . Photocurrent transient data showed that, even with a thick layer of ALD- SnO_2 , the addition of catalyst decreases photoactivity, Figure S3.8.

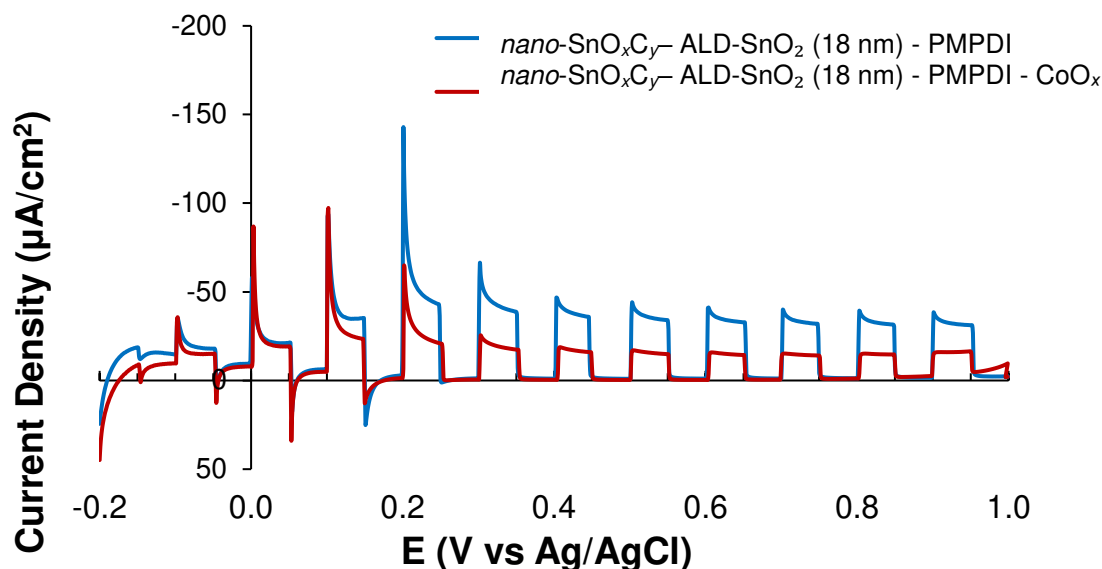


Figure S3.8. Photocurrent transients for *nano*-SnO₂/ALD-SnO₂(18 nm)/PMPDI (blue), and *nano*-SnO₂/ALD-SnO₂(18 nm)/PMPDI/CoO_x (red) anodes. Scans were done from -0.2 to +1.0 V vs Ag/AgCl with 5 second light dark transients.

Although a thicker coat of SnO₂ by ALD could conceivably overcome the C impurity filled *nano*-SnO_xC_y, the results show that the undesired recombination kinetics throughout the *nano*-SnO_xC_y cannot be overcome with an 18 nm thick ALD-SnO₂ coating. As noted in the main text, the results suggest that, instead, future research developing superior, carbon-free syntheses of SnO₂ and other M_xO_y nanoparticles is a better focus of additional research resources and effort.

S3.6. PMPDI Concentration Calculations on *nano*-SnO_xC_y and planar ALD-SnO₂ Anodes

In order to better understand the difference in the amount of dye on the anodes, we estimated the amount of PMPDI on a given anode. Previous work determined the molar extinction of PMPDI in aqueous solution to be ca. 22,000 M⁻¹/cm⁻¹ at 500 nm, the λ_{max} of the dye.¹ Herein, as in previous calculations, we assumed the extinction coefficient is roughly the same for PMPDI adsorbed on SnO₂ as PMPDI in aqueous solution. As before, we found the

absorbance of the dye at $\lambda_{\max}$, and after subtracting off the spectrum from an undyed *nano-SnO_xC_y* anode of the same thickness, to be Absorbance = 1.8, a typical value observed for all *nano-SnO_xC_y* anodes. This yields a concentration of ca. 0.14 mol PMPDI per L *nano-SnO_xC_y*. Using the anodes dimensions of $1.3 \text{ cm}^2 \times 6 \text{ }\mu\text{m}^1$, standard values for the anodes studied herein, we determined there to be 1.0×10^{-7} mol PMPDI, or 6.6×10^{16} molecules of PMPDI.

For ALD-SnO₂/PMPDI anodes, the same calculations were carried out on a representative sample. Typical absorbance of the dye at $\lambda_{\max}$, and after subtracting off the spectrum from an undyed ALD-SnO₂ anode of the same thickness, was determined to be 0.019 by UV vis. This results in a concentration of ca. 0.48 mol PMPDI per L ALD-SnO₂. Using the area of 1.3 cm^2 and a thickness of ALD-SnO₂ of 18 nm, which corresponds to 3.7×10^{-10} mol PMPDI, or 2.3×10^{14} molecules of PMPDI.

In order to determine the molar ratio of C to Sn to PMPDI in the *nano-SnO_xC_y*/PMPDI system, the moles of tin were calculated. The unsintered precursor *nano-SnO_xC_y* paste is 11 wt.% SnO₂. An unsintered anode (area 1.3 cm^2 , a typical size) therefore has 9.2 mg of unsintered precursor *nano-SnO_xC_y* paste doctor bladed onto it in a typical deposition. This means 1.0 mg of SnO₂, or 6.8×10^{-7} mol SnO₂, are added in a typical deposition. Once sintered, there then would be 1.5×10^{-7} mol C, per the discussion of the tin to residual carbon ratio in Section S3.1. This means in the *nano-SnO_xC_y* there is a molar ratio of 6.8 Sn: 1.5 C: 1.0 PMPDI.

S3.7. Oxygen Detection by Generator–Collector Method

Oxygen generation was measured as previously described.^{1,3–5} Planar ALD-SnO₂/PMPDI/CoO_x anodes were found to have an increased Faradaic Efficiency for WOC than the previously reported value for the *nano-SnO_xC_y*/PMPDI/CoO_x system, $45 \pm 6\%$ vs $31 \pm 7\%$

respectively. However, the ALD-SnO₂/PMPDI/CoO_x do display a significantly lower photocurrent, and thus oxygen generation, than their nanostructured counterparts (Figure S3.9). We hypothesize this relatively low, below 50%, Faradaic efficiency is likely due in part to some combination of oxidation of water to H₂O₂ instead of O₂, dye-degradation (though dye losses are minimal over the time scale studied), and perhaps the oxidation trace impurities in the buffer or Cl⁻ leached from the reference electrode. Previously we have published ca. 90 minute photoanode performance² demonstrating 78% decay in photocurrent generation and a the ca. 11% decrease in O₂ generation over 1200 seconds. We do not see significant dye loss here, or in our previous systems, and have previously shown mathematically that the observed current decrease *cannot* be attributed to dye loss.¹

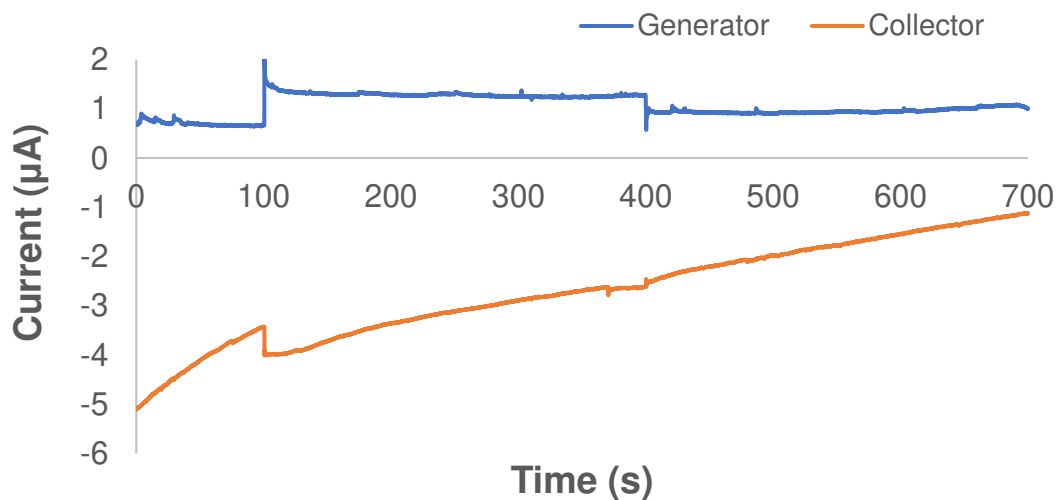


Figure S3.9: ALD-SnO₂/PMPDI/CoO_x Generator – Collector data where the generator working ALD-SnO₂/PMPDI/CoO_x anode (blue) of interest was held at +0.2 V vs Ag/AgCl to produce oxygen and the collector FTO was held at -0.6 V vs Ag/AgCl to reduce O₂. The device placed in pH 7, 0.1 M KPi buffer and was held in the dark for 100 seconds, illuminated as described in the main text for 300 seconds, and then was held in the dark for 300 more seconds.

S3.8. Planar Anodes Raw Data

The photocurrent of planar ALD-SnO₂/PMPDI was measured both with and without CoO_x, Figure S3.10. Slight baseline drift was seen, which was noticeable due to low photocurrents. Both the slight baseline drift and the background current from FTO are corrected for (removed) in the data presented in the main text, Figure 8, but are displayed in full below so that the reader can obtain a feel for the baseline drift. When the planar photoanode performance is scaled up for comparison to the *nano*-SnO_xC_y anodes, the background current becomes exaggerated, though the value does not truly represent the background current or the anode's photoperformance in the dark.

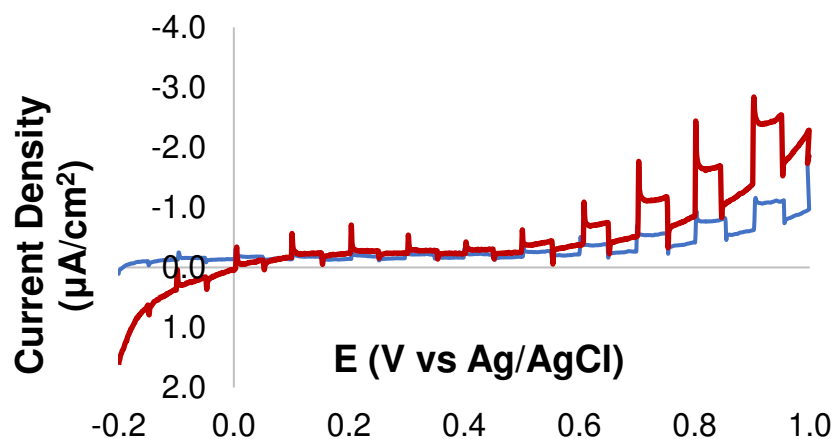
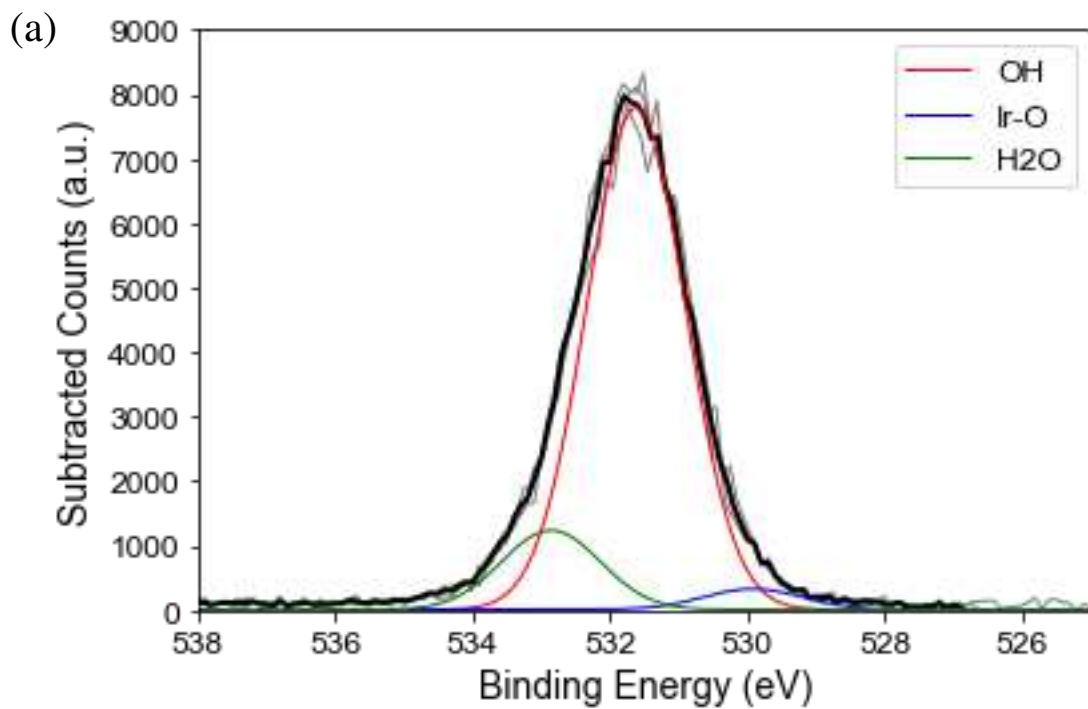


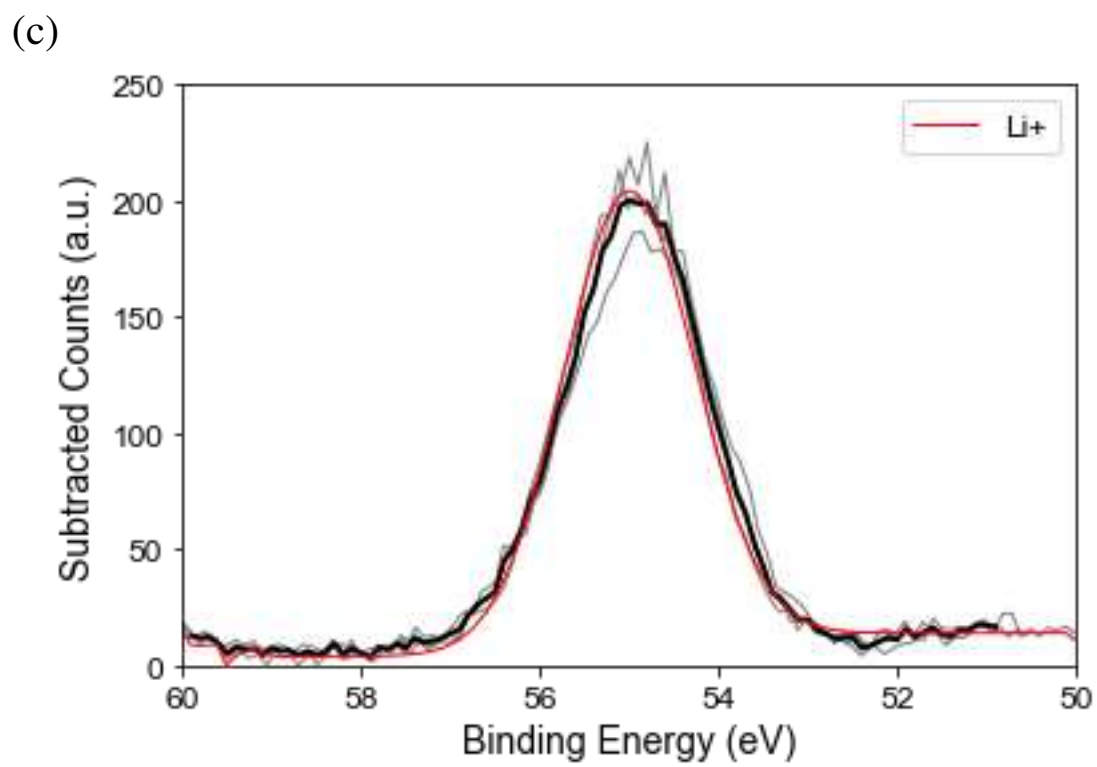
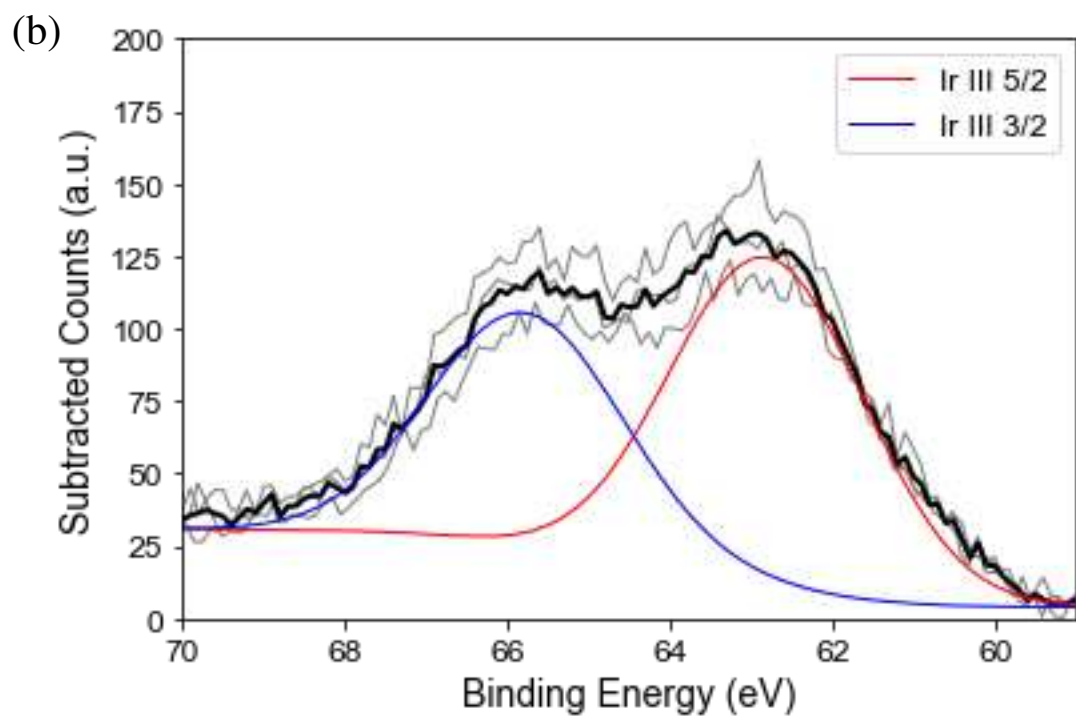
Figure S3.10. Photocurrent transients for ALD-SnO₂(5nm)/PMPDI (blue) and ALD-SnO₂(5nm)/PMPDI/CoO_x (red), anodes. Scans were done from -0.2 to +1.0 V vs Ag/AgCl with 5 second light dark transients. Note background currents and current from background FTO are included here.

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S4.1. XPS of Li-IrO_x





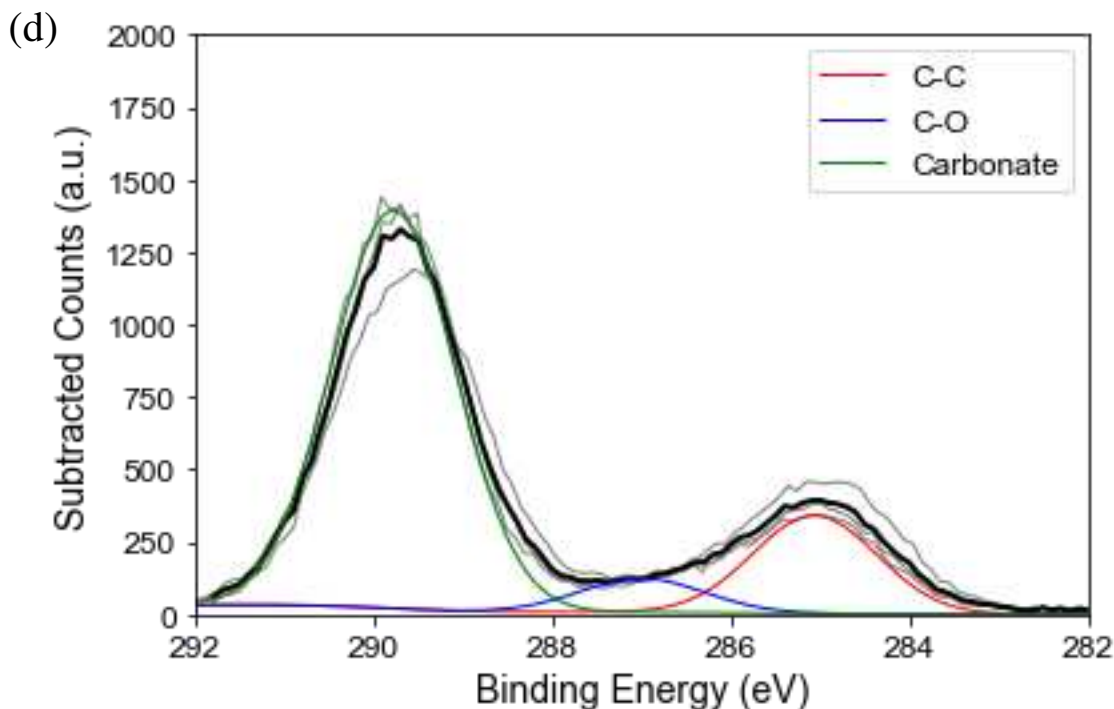


Figure S4.1. Representative high resolution XPS scans of (a) O 1s electron, (b) Ir 4f, (c) Li 1s, and (d) C 1s drop on Li-IrO_x casted on FTO at 120 °C. For each XPS figure, the light grey spectra are raw data for each replicate and the black spectrum is an average of all replicates. Note that the fit peaks shown correspond to one of the raw data grey spectrum deemed to be similar to the average. Satellite peaks for iridium were not fit as they were deemed unnecessary for a complete and accurate fit.

S4.2. Further Discussion of Deposition of Li-IrO_x

In order to better replicate the previous work using Li-IrO_x, the Li-IrO_x catalyst was sprayed onto the device using a nebulizer.¹ A handheld nebulizer (Hudson RCI, Micro Mist) was used with air to deposit 1.0 mL a 95:5 v/v ethanol: water mixture containing 2.5 mg of Li-IrO_x. The back end of the device covered using parafilm to minimize losses of the deposition solution. The air pressure used was the minimum value sufficient to nebulize the solution. This value was not measured but the manufacturer reports this value to be 8 liters per minute. As the device aperture was larger than the anode, a short channel was constructed out of parafilm in the shape and size of the anode in order to ensure all of the solution was deposited onto the anode in the

correct area. Additionally, it was thought that this would minimize inconsistency that could occur if manual scanning across the anode with the nebulizer was done. The anode was then heated to 120 °C under air. True catalyst loading was not determined.

S4.3. Electrochemically-Active Surface Area Correction

In order to understand how the electrochemically-active surface area of the planar and 3-dimensional SnO₂ anodes compares double layer capacitance was used. It was assumed that the two types of SnO₂, nano and ALD SnO₂, would have the same electrochemical response. Since the planar SnO₂ anodes have a known geometric surface area, measured from photos of the anodes using ImageJ, which is equivalent to the electrochemically active surface area, a scalar value could be determined. Cyclic voltammetry scans were taken of planar anodes at varying scan rates and the current at +0.4 V vs Ag/AgCl was plotted with scan rate (Figure 4.5, Chapter IV) Using eq. S4.1², where i_c is current, A is area, C_d is double layer capacitance, and v is scan rate, the slope of this line was determined to be directly proportional to the double layer capacitance response.

$$|i_c| = AC_d v \quad (S4.1)$$

The double layer capacitance response determined from the slope can then be divided by the geometric surface area of the planar anodes, giving a scalar value representing the electrochemically active surface area/ the geometric surface area.

To compare the anodes made with planar SnO₂ by ALD to the nano-SnO_xC_y anodes made in house, a correction using dye absorbance was made on photocurrent transient plots with the addition of the sacrificial reductant hydroquinone, H₂Q, in order to ensure data was not overcorrected. However, it is not known if the dye absorbance or the electrochemically-active surface area is a more accurate representation of the true system. Thus, data was also corrected using the higher,

1:187 planar to nanostructured, electrochemically-active surface area value as well (Figure S4.2). The data from the planar SnO_2 anodes corrected using the electrochemically-active surface area is significantly higher than the highest values observed in any nanostructured system. Likely, the true value of the corrected anodes is located somewhere between the two corrected values but certainly the planar SnO_2 outperforms the nano- SnO_xC_y when comparing based on dye absorbance or electrochemically-active surface area.

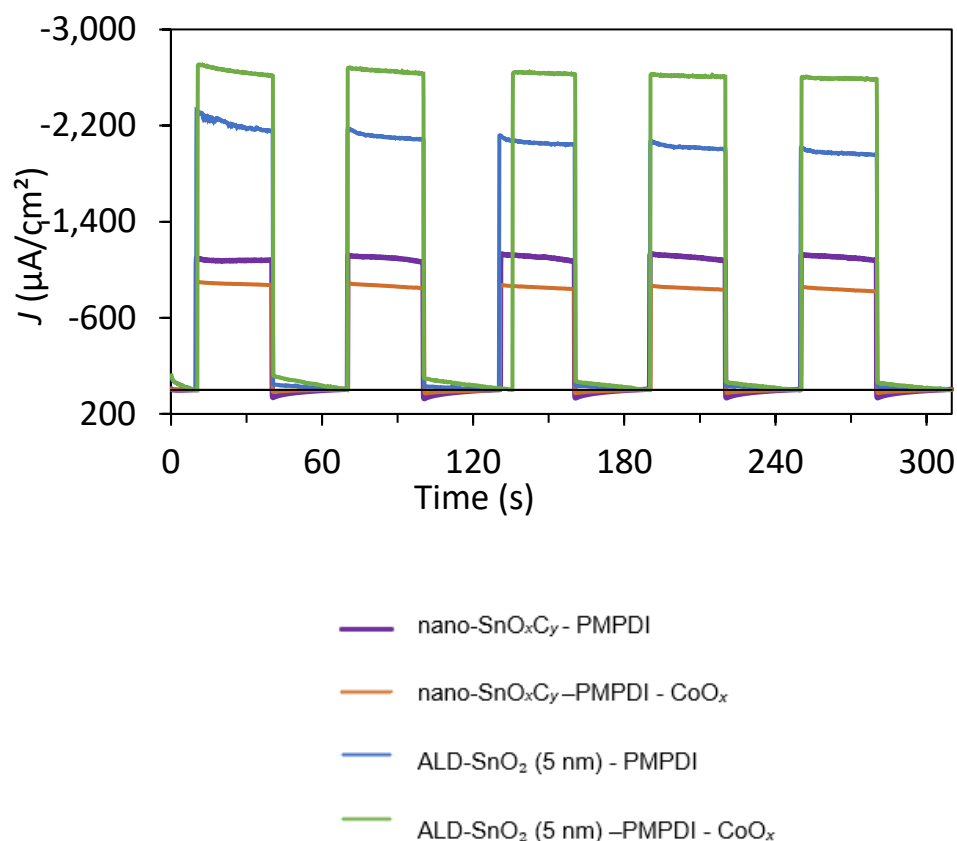


Figure S4.2. J - t transients in the presence of 20 mM H_2Q sacrificial reductant, with background dark current subtracted, at +0.2 V vs Ag/AgCl in pH 7, 0.1 M KPi buffer with 30 s light/dark transients where purple is nano- SnO_xC_y /PMPDI, red is nano- SnO_xC_y /PMPDI/ CoO_x , blue is ALD- SnO_2 (5 nm)/PMPDI, and green is ALD- SnO_2 (5 nm)/PMPDI/ CoO_x . Both planar (blue and green) anodes are corrected to match the electrochemically-active surface areas of the nanostructured anodes.

When the planar photoanode performance is scaled up for comparison to the nano-SnO_xC_y anodes, the background current becomes exaggerated, though the value does not truly represent the background current or the anode's photo performance in the dark.

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LIST OF ABBREVIATIONS

ALD	atomic layer deposition
AM1.5G	air mass 1.5 global standardized solar irradiance
APCE	absorbed photon-to-current efficiency
CoO _x	amorphous cobalt oxide
CV	cyclic voltammetry, cyclic voltammogram
D–A	sensitizer dye composed of electron-donor and acceptor functional groups
D- π -A	sensitizer dye composed of electron-donor and acceptor functional groups separated by a π -conjugated bridge
DS-PEC	dye-sensitized photoelectrolysis cell
DSSC	dye-sensitized solar cell
EDX/EDS	electron-dispersive X-ray spectroscopy
FTO	fluorine-doped tin oxide coated glass
HER	hydrogen-evolving reaction
H ₂ Q	hydroquinone, 1,4-dihydroxybenzene
IPCE	incident photon-to-current efficiency
ITO	indium-tin oxide coated glass
KPi	potassium phosphate buffer (inorganic)
LHE	light-harvesting efficiency
M _x O _y	metal oxide
NHE	normal hydrogen electrode
NP	nanoparticle
OER	oxygen-evolving reaction
OPV	organic photovoltaic
OSC	organic semiconductor
OTF	organic thin-film
PDI	a perylene diimide derivative
PEC	photoelectrolysis cell
PMPDI	N,N'-bis(phosphonomethyl)-3,4,9,10-perylenediimide
PV	photovoltaic
RHE	reversible hydrogen electrode
Ru–bda	a class of WOCatalysts based on the [Ru(bda)(pic) ₂] structural motif
Ru–pdc	a class of WOCatalysts based on the [Ru(pdc)(pic) ₃] structural motif
SC	semiconductor
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
UV-vis	UV-visible spectroscopy

WOC	water-oxidation catalysis
WOCatalyst	water-oxidation catalyst
XPS	X-ray photoelectron spectroscopy