

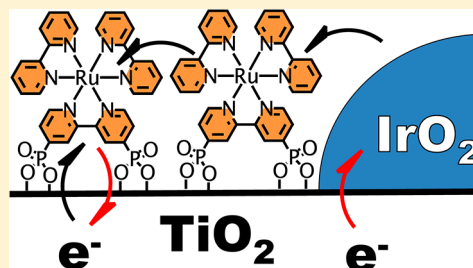
Photovoltage Effects of Sintered IrO₂ Nanoparticle Catalysts in Water-Splitting Dye-Sensitized Photoelectrochemical Cells

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S Supporting Information

ABSTRACT: Water-splitting dye-sensitized photoelectrochemical cells (WS-DSPECs) utilize high surface area TiO₂ electrodes functionalized with light absorbing sensitizers and water oxidation catalysts. Because water splitting requires vectorial electron transfer from the catalyst to the sensitizer to the TiO₂ surface, attaching both sensitizer and catalyst to TiO₂ in the correct sequence and stabilizing them under photoelectrochemical conditions has been a challenging problem. Rutile-phase IrO₂ nanoparticles can be deposited directly on the TiO₂ electrode by adsorbing citrate-capped amorphous IrO_x and then sintering at 450 °C. Electrodes functionalized with these nanocrystalline particles show higher activity than those made from ligand-capped amorphous IrO_x without sintering. In the WS-DSPEC, the Coulombic efficiency for oxygen evolution from the sintered nanoparticle photoelectrodes was near unity. The loading of colloidal IrO_x and IrO₂ particles onto the porous TiO₂ electrodes was quantified by neutron activation analysis. Photovoltage measurements suggest that at high catalyst loading the dominant charge recombination pathway is from photoinjected electrons to IrO₂.



INTRODUCTION

Inspired by dye-sensitized solar cells, water-splitting dye-sensitized photoelectrochemical cells (WS-DSPECs) are attractive as a possible technology for converting solar energy to fuel. Like dye-sensitized solar cells, WS-DSPECs capture visible light using a low-cost mesoporous TiO₂ film functionalized with a molecular sensitizer. WS-DSPECs employ a water oxidation catalyst instead of a reversible redox couple such as I[−]/I₃[−] to regenerate the oxidized dye. Water is oxidized with the release of protons at the anode catalyst, and proton reduction at the cathode completes the circuit. Both heterogeneous and homogeneous water oxidation catalysts have been shown to function in WS-DSPECs.^{1–9}

Because the quantum yield for charge injection into the TiO₂ conduction band approaches unity,^{1,3,4} WS-DSPECs have the potential to be efficient devices for solar fuel conversion. However, stable attachment of dye and catalyst to TiO₂ and controlling the vectorial electron-transfer pathway have been significant challenges in WS-DSPECs. Hanson et al.¹⁰ demonstrated that under aqueous conditions, sensitizers attached to TiO₂ through carboxylic acid groups undergo rapid hydrolysis in the dark. Phosphonate-functionalized sensitizers showed better adhesion to TiO₂ in the dark, but under illumination these sensitizers also desorbed from TiO₂. A recent paper explored linking high-potential porphyrins to TiO₂ with acetylacetonate and hydroxamic acid anchors in addition to carboxylic and phosphonate moieties, but the linkage stability was not tested under photoelectrochemical conditions.¹¹ Gao et al. used a silane linkage to anchor a molecular

ruthenium water oxidation catalyst and reported a more stable, high current density under illumination.⁵

As an electrocatalyst for water oxidation, iridium oxide offers a high turnover rate and low overpotential across a wide pH range.^{12–14} One strategy for incorporating colloidal iridium oxide into WS-DSPECs is to directly couple sensitizer molecules to the nanoparticle. The composite particle is then attached to the TiO₂ electrode through a carboxylic or phosphonic acid group on the dye.^{2,3,15} While this strategy positions dye molecules between the catalyst and the TiO₂ surface, such assemblies are challenging to make and their dye-to-catalyst ratios are relatively low. An alternate strategy is to separately adsorb the sensitizer and catalyst onto the high surface area TiO₂ electrode. In this synthetically simpler approach, high dye-to-catalyst ratios are possible, following the antenna–reaction center principle of natural photosystems. Recently we used this strategy with an iridium oxide catalyst functionalized with a biomimetic tyrosine-histidine electron-transfer mediator and obtained a 2.3% internal quantum efficiency for water splitting.⁹ However, these amorphous IrO_x particles were still attached to the TiO₂ surface through carboxylic and phosphonic acid groups. It is known that crystalline rutile IrO₂ has an activity per surface iridium atom higher than that of citrate-capped amorphous IrO_x under

Special Issue: Michael Grätzel Festschrift

Received: January 17, 2014

Revised: April 7, 2014

Published: April 9, 2014



similar photochemical conditions.^{12,16} Thus, we sought to develop a strategy for eliminating ligand capping of IrO₂ nanoparticles in the WS-DSPEC. Here we describe a new strategy for preparing small (~2 nm) particles of crystalline IrO₂ that are sintered directly onto the porous TiO₂ film. Significantly higher photoelectrochemical activity is observed relative to ligand-capped IrO_x particles. The photocurrent is not monotonic with catalyst loading, but instead peaks at intermediate loading. Photovoltage measurements suggest that electron transfer from the conduction band of the TiO₂ to the IrO₂ particles is the dominant loss pathway in these systems.

■ EXPERIMENTAL DETAILS

Bis(2,2'-bipyridine)(4,4'-diphosphonato-2,2'-bipyridine)-ruthenium bromide was synthesized as previously reported.¹⁷

Synthesis of Citrate-Capped IrO_x. Sodium hydrogen citrate sesquihydrate (0.6 mmol) was dissolved in 95 mL of 18 MΩ Nanopure H₂O. The pH was adjusted to 5 with 0.5 M NaOH. K₂IrCl₆ (0.1 mmol) was added, and the solution was refluxed at 90 °C. After 1 h, the temperature was decreased to 75 °C and the pH adjusted to 6.2. Using 0.5 M NaOH, the pH of the solution was maintained between 6.0 and 6.2 for 5 h resulting in a deep blue solution. The final volume was adjusted to 100 mL, and the room-temperature solution stirred with 5 g of Dowex 1 × 8 50 ion-exchange resin activated by 10 min of stirring in 0.1 M NaOH.

Photoanode Preparation. All electrodes were prepared on 8 Ω/cm² fluorine-doped tin oxide-coated glass (FTO-glass, Hartford Glass Company). A colloidal suspension of TiO₂ prepared as previously described¹⁸ was deposited onto the FTO-glass via the doctor blade method. Three layers of Scotch tape acted as a 175 μm thick spacer layer with the area of the film approximately 1 cm². The films were sintered at 300 °C for 20 min, 350 °C for 10 min, and 450 °C for 30 min under flowing air. After being cooled, the electrodes were soaked in solutions of citrate-capped IrO_x colloid at total Ir concentrations between zero and 400 μM for 14 h. To prepare sintered catalyst electrodes, these electrodes were then annealed in air for 3 h at 450 °C. Insulated silver-plated copper wire was attached to the electrode using silver paste (DuPont CP4922N-100), and contacts were protected using white epoxy (Loctite IC Hysol). Electrodes were sensitized by soaking in the dark in 100 μM bis(2,2'-bipyridine)(4,4'-diphosphonato-2,2'-bipyridine)ruthenium bromide in ethanol for 22 h at room temperature then rinsed thoroughly with ethanol and dried under a stream of N₂. Following dye deposition, electrodes were kept in the dark until use. Electrodes prepared without sintered catalyst particles were annealed for 3 h at 450 °C before soaking in citrate-capped IrO_x.

Characterization of Photoanodes. Iridium loading into the TiO₂ film was determined by neutron activation analysis performed at the University of Wisconsin-Madison Nuclear Reactor. TiO₂ films loaded with citrate-capped IrO_x at various concentrations were prepared on FTO then scraped off mechanically and loaded into 2/5 dram polyvials. Typically 10 mg of powder was analyzed at each iridium loading. Each sample was irradiated in the reactor for 2 h, and γ radiation emissions were collected 19 days after irradiation using a high-purity germanium detector.

Scanning transmission electron microscopy (STEM) was performed on a JEOL 2010F transmission electron microscope

operated in Z-contrast mode. A TiO₂ film loaded and sintered from 100 μM citrate-capped iridium oxide was mechanically scraped off the FTO and suspended in isopropanol by sonication. The suspended powder was then dropcast onto a TEM grid and allowed to dry.

The surface area of the sintered TiO₂ films was determined by mechanically scraping off a 100 cm² film on FTO. The powder was then analyzed by Brunauer–Emmett–Teller (BET) analysis on a Micromeritics ASAP 2020 instrument for surface area and average pore diameter. Profilometry of TiO₂ films was performed on a KLA-Tencor P-16+ Profilometer. X-ray powder diffraction (XRD) patterns were collected on a PANalytical Empyrean X-ray diffractometer.

Photoelectrochemical Measurements. The sensitized working electrode was placed in a custom H-cell fitted with a quartz cuvette. A Ag/AgCl/NaCl (3M) ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.597 \text{ V}$) reference electrode was placed in the same compartment, and a platinum mesh counter electrode placed in the adjoining compartment. The cell was sealed with rubber septa, and the electrode leads were passed through the septa. The compartment containing the cathode was purged with 5% hydrogen in argon, and the anodic compartment with air.

Open circuit voltage (V_{oc}) measurements were made under illumination with a battery-powered voltmeter. This arrangement avoided cross-talk of ground leads when the working electrode potential or current was controlled by an AC-powered potentiostat. Bulk photoelectrolysis measurements were performed at +100 mV versus Ag/AgCl for 10 min under illumination using a Nuvant EZ-Stat Pro potentiostat. The illumination source was a 150 W Newport Oriel lamp fitted with AM0, AM1.5, and 410 nm long-pass filters.

Electrochemical impedance spectroscopy (EIS) was performed in an identical configuration, except that unsensitized electrodes were used and the 410 nm long-pass filter was removed. A Metrohm Autolab potentiostat with an FRA32 M module made EIS measurements under galvanostatic control. The measurements were made under open-circuit conditions with a 3 μA perturbation from 1 MHz to 0.1 Hz.

Amperometric Determination of the Coulombic Efficiency of Oxygen Evolution. Current efficiency for oxygen evolution was calculated using a planar platinum collector electrode as previously described.³ The bare FTO on the photoanode was masked by 25 μm thick polyimide tape, leaving the 1.0 cm² square sensitized, catalyst-functionalized TiO₂ film. A platinum collector electrode was placed in front of the photoanode. The polyimide tape served as a spacer between the two electrodes, which were bound together with a strip of parafilm at the top and bottom of the electrodes. Both electrodes were placed into the anodic compartment of the H-cell, which was sealed with rubber septa and purged with Ar. A bipotentiostat (Pine Instrument Company, AFCBP1 Bipotentiostat) was used to apply a potential bias to the two working electrodes; the sensitized TiO₂ film was held at +100 mV versus Ag/AgCl, while the collector electrode was poised at −640 mV versus Ag/AgCl for oxygen reduction. The collection efficiency of the collector electrode was determined by using a second platinum electrode in place of the photoanode in an identical configuration poised at 1.3 V versus Ag/AgCl.

■ RESULTS AND DISCUSSION

Characterization of Citrate-Capped IrO_x. The absorption spectrum of the as-prepared citrate-capped IrO_x colloid shows a broad visible absorbance, with a peak absorbance at

approximately 580 nm that is generally assigned to Ir(IV).^{19,20} There is also a strong absorbance below 450 nm that is likely some combination of absorbance by Ir(III) and light scattering. This mixture of Ir(III) and Ir(IV) is generally consistent with other examples of colloidal IrO_x.^{12–14,21} No impurity peak was observed at 310 nm (Figure S1 of Supporting Information). That peak is ascribed to a monomeric iridium hydroxide species, and its absence indicates complete conversion of the IrCl₆^{2–} precursor to IrO_x.^{9,14} TEM analysis of the IrO_x particles gave an average diameter of 1.8 ± 0.1 nm (Figure S2 of Supporting Information), consistent with previous examples of ligand-capped IrO_x.^{16,199}

To explore the interaction between the IrO_x and the citrate stabilizing ligand, FTIR spectroscopy was performed on a dry sample of particles (Figure S3 of Supporting Information). A drop of the purified citrate-capped IrO_x solution was placed on an ATR attachment then dried for several hours under a steady stream of N₂. The control sample of sodium hydrogen citrate sesquihydrate shows strong carbonyl stretches at 1733 and 1602 cm^{–1}, which can be assigned to carboxylic acid and carboxylate groups, respectively. A third strong absorbance at 1407 cm^{–1} can also be assigned to the carboxylate group. In the IR spectra of the IrO_x particles, the carboxylate absorbances are shifted to 1578 and 1396 cm^{–1}, indicating the citrate ligand is bound to the IrO_x particle. In addition, the peak at 1733 cm^{–1} has disappeared, indicating that the carboxylic acid groups on the citrate ligand are deprotonated.

Characterization of Photoanodes. Post-sintering, the porous TiO₂ films used in this study were typically 12 μm thick as verified by profilometry. The film consists of an interconnected network of approximately 20 nm diameter anatase TiO₂ particles with a surface area of 98.2 ± 0.5 m²/g and average pore diameter (determined from the Barrett–Joyner–Halenda (BJH) model) of 19.5 ± 0.9 nm. X-ray diffraction of catalyst-free and citrate-capped functionalized TiO₂ films on FTO showed peaks at 25.4° and 26.5° that can be assigned to the (101) reflections of anatase TiO₂ and the (110) reflection of rutile FTO (Figure S4 of Supporting Information). For electrodes containing sintered catalyst particles, an additional broad reflection at 28.1° was also observed, which is assigned to the (110) reflection of rutile-phase IrO₂.^{5,22}

XPS was used to further explore the state of the postsintered catalyst (Figure S5 of Supporting Information). Because the 3s peak of Ti overlaps the 4f peaks of Ir, sintered IrO₂ was prepared instead on a 300 nm thick film of SiO₂ on a silicon wafer. An IrO₂ standard showed a pair of peaks at 59.6 and 62.4 eV, corresponding to the 4f_{7/2} and 4f_{5/2} of Ir(IV). A dropcast film of citrate-capped IrO_x shows three distinct peaks at 62.1, 60.4, and 59.4 eV likely due to the amorphous colloid being a mixture of Ir(III) and Ir(IV). The sintered sample shows two broad peaks at 60.2 and 62.9 eV, suggesting that Ir(IV) dominates the spectrum. Broadening of the peaks may be due in part to a small, unresolved amount of Ir(III) and low signal strength in the sintered sample.

From the XRD and XPS data, we conclude that the sintered catalyst particles are most likely crystalline IrO₂ in the rutile phase. The high sintering temperature (450 °C) in air drives the formation of the crystalline material, which is consistent with earlier observations of the formation of rutile IrO₂ at temperatures above 400 °C in the presence of oxygen.^{23,24}

Post-sintering particle size was measured by scanning transmission electron microscopy (STEM). Figure 1 shows a

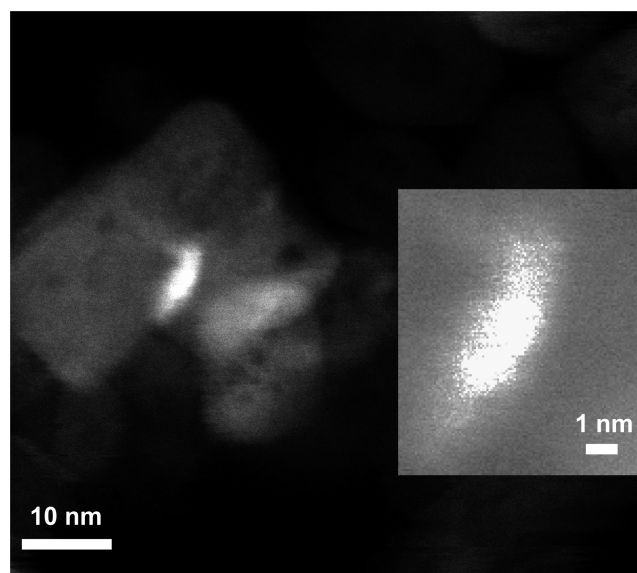


Figure 1. STEM image of IrO₂ particles on TiO₂. Inset: magnified image with contrast adjusted to show particle size and shape.

STEM micrograph of sintered IrO₂ on TiO₂ in Z-contrast mode and clearly shows a bright spot on the TiO₂. The bright region is magnified in the inset and the contrast reduced by half, revealing two patches approximately 2 nm in diameter each. In Z-contrast mode heavier elements appear brighter, and the image shows that sintered iridium oxide retains the small particle size of the stabilized colloid in solution. No aggregates of IrO₂ were observed, suggesting the particles are well-distributed. Because the catalyst loading was very low, IrO₂ particles on TiO₂ were difficult to find by STEM, and this prevented us from obtaining a statistical analysis of particle size.

Neutron activation analysis of the catalyst-functionalized electrodes (Figure 2) reveals a roughly linear correlation between the concentration of iridium in the deposition solution and the amount of iridium deposited onto the electrode. The coverage is plotted in units of picomoles of iridium per unit

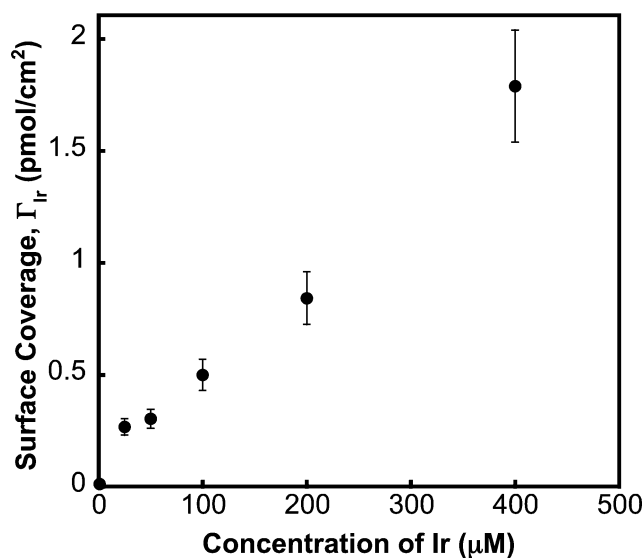


Figure 2. Neutron activation analysis of TiO₂ functionalized with citrate-capped IrO_x. Deposited coverage (Γ) is plotted in picomoles of Ir per total surface area of the TiO₂ film.

area of the high surface area electrode. Over the concentration range explored, the catalyst nanoparticles occupy a very small fraction of the TiO_2 surface, so this linear behavior is consistent with an equilibrium adsorption isotherm of the precursor particles. We can estimate from the volume of the rutile unit cell that each 2 nm diameter IrO_2 cluster contains approximately 130 Ir atoms. This means that even at the highest catalyst loading, the IrO_2 particles occupy only about 0.025% of the total TiO_2 surface area.

Post-sintering, the electrodes have a blue tint that becomes more distinct as the catalyst loading is increased. In the UV–vis spectra, a slight increase in absorbance can be observed, particularly at longer wavelengths (Figure S6 of Supporting Information). This can be assigned to the characteristic Ir(IV) absorbance, though a distinct IrO_2 spectrum could not be observed. After soaking in bis(2,2'-bipyridine)(4,4'-diphosphonato-2,2'-bipyridine)ruthenium bromide (100 μM in ethanol) for 22 h, the electrodes have a deep orange color and a significant increase in visible absorbance can be seen in the UV–vis (Figure 3) centered around 450–460 nm, which is

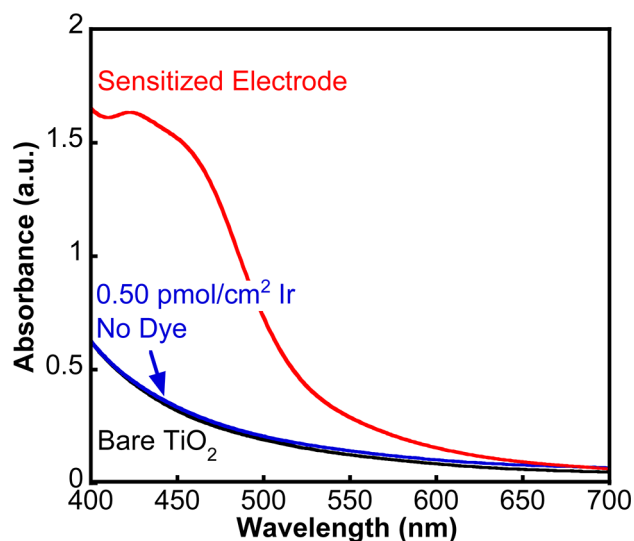


Figure 3. UV–vis spectra of TiO_2 electrodes on FTO: (1) bare TiO_2 , (2) post-sintering 0.50 pmol Ir/cm^2 , and (3) after sensitization with 100 μM bis(2,2'-bipyridine)(4,4'-diphosphonato-2,2'-bipyridine)-ruthenium bromide.

characteristic of bis(2,2'-bipyridine)(4,4'-diphosphonato-2,2'-bipyridine)ruthenium bromide. Post-sensitization, all electrodes had an optical density between 1.4 and 1.6.

Photoelectrochemical Performance of Electrodes.

Figure 4 shows the photocurrent generated from sensitized photoanodes functionalized with different coverages of sintered IrO_2 catalyst as well as unsintered citrate-capped IrO_x (0.50 pmol/ cm^2). Each curve is the average of three measurements. Photocurrent was measured over 10 min of illumination at an applied bias of +100 mV versus Ag/AgCl in a custom H-cell (Figure S7 of Supporting Information). All electrodes showed an initial current spike that rapidly polarized, a feature generally observed in WS-DSPECs. Over 10 min, the polarization was significant with final currents roughly 1 order of magnitude lower than the initial peak currents. Surprisingly, the best performing condition is prepared by soaking in 100 μM citrate-capped IrO_x then sintering to form IrO_2 (0.50 pmol Ir/cm^2). These samples briefly surpassed 225 $\mu\text{A}/\text{cm}^2$ before rapidly

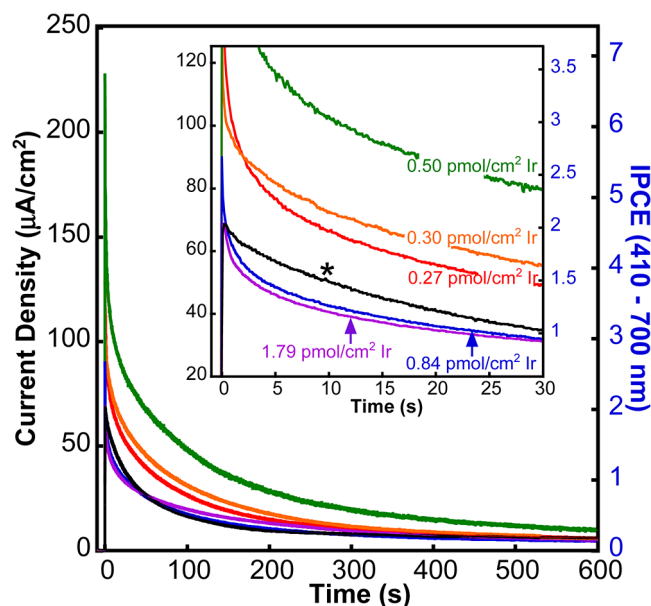


Figure 4. Bulk photoelectrolysis of sensitized, sintered IrO_2 (coverage in picomoles per square centimeter) and 0.5 pmol cm^{-2} IrO_x citrate-capped photoanodes (*) held at 100 mV versus Ag/AgCl in 100 mM pH 6.8 $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$; counter electrode is Pt mesh. Inset focuses on the first 30 s of the bulk photoelectrolysis traces.

polarizing. This current represents an incident photon-to-current efficiency (IPCE) of 6.75% when integrated from 410 to 700 nm. At higher iridium loadings, 0.84 and 1.79 pmol Ir/cm^2 , the photocurrent drops off significantly, with the 1.79 pmol Ir/cm^2 sample showing the lowest peak current (38 $\mu\text{A}/\text{cm}^2$) of any of the sintered IrO_2 samples. The two lowest coverages explored, 0.27 and 0.30 pmol Ir/cm^2 , gave higher photocurrents than the higher coverage samples, reaching peak currents of 154 and 129 $\mu\text{A}/\text{cm}^2$, respectively. Over the course of 10 min, the 0.30 pmol Ir/cm^2 electrodes were slightly more efficient, passing 12% more charge than those with 0.27 pmol Ir/cm^2 . Electrodes prepared from unsintered 100 μM citrate-capped IrO_x showed significantly lower photocurrent than those made with sintered nanoparticles. This is not unexpected, as we previously noted that ligand-capped particles exhibit activity lower than that of IrO_2 .^{9,12,16}

To understand the difference in photoelectrochemical performance of the sintered catalyst samples, the photovoltage was measured as a function of Ir coverage (Figure 5). The photovoltage results mirror the observed photocurrents for the different anodes. At the highest coverage of sintered catalyst, the lowest photovoltage (1013 ± 10 mV) was observed, and the highest photovoltage (1070 ± 13 mV) was found with sintered electrodes of intermediate coverage (0.50 pmol/ cm^2). This suggests that the differences in photocurrents between the different sintered catalyst coverages are correlated with the photovoltage at each photoanode.

For each value of the Ir coverage, the photovoltage was measured as the difference between the open-circuit potential of the photoanode under illumination (relative to a Ag/AgCl reference electrode) and the potential of the $\text{O}_2/\text{H}_2\text{O}$ couple at pH 6.8 (0.631 V versus the same reference) (Figure S8 of Supporting Information). These measurements gave values in the range of 900–1100 mV, consistent with earlier observations that a ≥ 300 mV applied bias is needed to drive water splitting in the WS-DSPEC.^{2,9} The condition of electrochemical

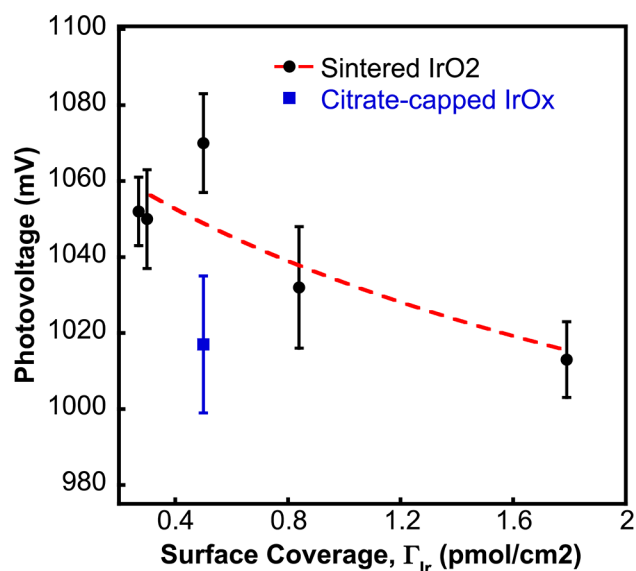


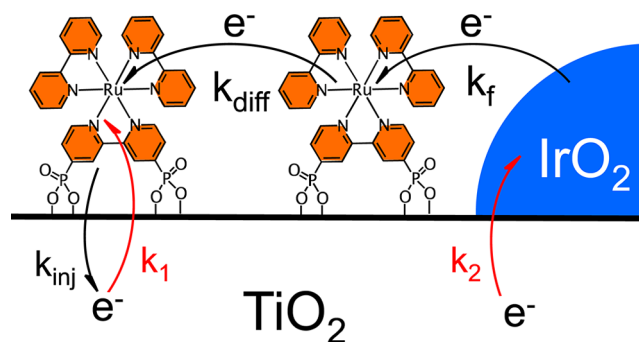
Figure 5. Photovoltage of sensitized electrodes as a function of Ir surface coverage. Dashed line shows a fit to the data using eq 1.

equilibrium implies that the potential of an electrode in the dark should equal the potential of the contacting solution. In the anode compartment of the cell, the potential of the air-saturated solution is fixed by the $\text{O}_2/\text{H}_2\text{O}$ couple. Experimentally, we find that after an initial polarization, the steady-state potential of the anode in the dark is approximately 0 V versus Ag/AgCl, approximately 630 mV negative of the $\text{O}_2/\text{H}_2\text{O}$ couple. This implies that the dark TiO_2 electrode is not in equilibrium with the $\text{O}_2/\text{H}_2\text{O}$ couple and that its potential is fixed by other dark redox processes, such as reduction of O_2 by electrons in deep traps. Under illumination, Ru(III) is generated at the TiO_2 surface and electrons are transferred to Ru(III) from the IrO_2 catalyst, which in turn drives the water oxidation reaction. Because the potential of the $\text{O}_2/\text{H}_2\text{O}$ couple is fixed, the open-circuit voltage of the electrode can be defined as the potential difference between the electrode in the light (measured against the Ag/AgCl reference) and the potential of the $\text{O}_2/\text{H}_2\text{O}$ couple in the contacting solution.

Under illumination, the electrode potential (i.e., the Fermi level of electrons in TiO_2) is determined by the balance of electron injection and electron recombination from the conduction band and sub-band gap trap states.²⁵ At all catalyst coverages, the rate of electron injection can reasonably be approximated as the same because all electrodes are sensitized to the same optical density and tested under identical illumination conditions. At higher catalyst coverage, we would anticipate that the regeneration of the dye would be faster with more catalytic sites available. This in turn should lead to higher photovoltages and photocurrent. That the photovoltage and photocurrent decrease at higher catalyst coverage suggests that the recombination rate must be increasing. Valence band electrons can recombine with oxidized Ru(III) centers on the TiO_2 surface (k_1 in Scheme 1).

Under illumination, the concentration of oxidized Ru(III) is determined by the relative rates of electron injection, recombination of Ru(III) with valence band electrons, and electron transfer from IrO_2 to Ru(III). Again, under identical sensitization and illumination conditions, the concentration of Ru(III) should either be the same for all catalyst coverages or, if the rate of electron transfer from IrO_2 is sufficiently rapid,

Scheme 1. Illustration of Electron Injection (k_{inj}), Cross-Surface Electron Transfer (k_{diff}), and Regeneration of Oxidized Dye by the IrO_2 Catalyst (k_{f}); Back Electron-Transfer Reactions to the Oxidized Dye (k_1) and to the IrO_2 Catalyst (k_2) are Shown in Red



should decrease as catalyst coverage increases. By decreasing the concentration of Ru(III), we would anticipate fewer electron recombination sites and a higher photovoltage rather than the decrease that is observed.

With IrO_2 particles sintered directly to the TiO_2 , electron transfer from the conduction band or trap states of the TiO_2 to the IrO_2 particles (k_2 in Scheme 1) can become an important charge recombination reaction. To probe this pathway, unsensitized films of TiO_2 on FTO functionalized with sintered IrO_2 catalysts were studied under UV illumination using electrochemical impedance spectroscopy (EIS). This approach removes effects related to the oxidized dye, such as back electron transfer and desorption, that might complicate the analysis. Following the analysis of Wang et al.²⁶ as well as that of Fabregat-Santiago et al.,²⁷ the lifetime of the electron in the TiO_2 can be obtained from the phase plot of EIS data. The lifetime is given as the inverse of the frequency of the peak phase in the 10–100 Hz region.²⁶ The calculated lifetimes are shown as a function of iridium concentration in the deposition solution in Figure 6. When no iridium was present, a lifetime of 6.25 ms was observed. As the coverage of iridium increased, the

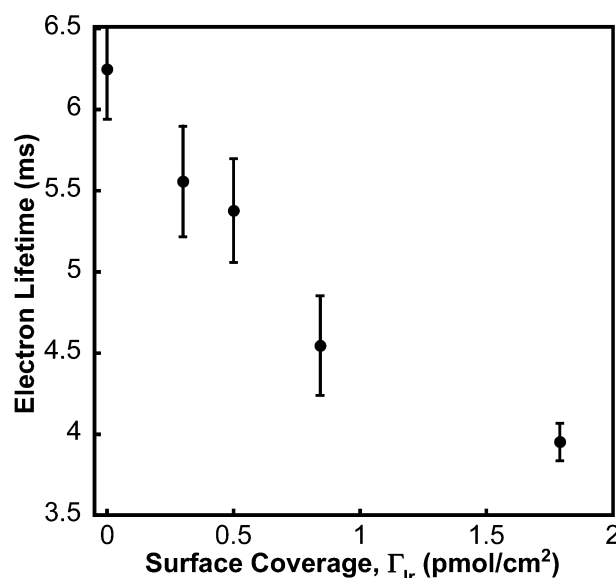


Figure 6. Electron lifetime in sintered $\text{IrO}_2/\text{TiO}_2$ electrodes calculated from the phase plot of the EIS spectra as a function of Ir coverage.

lifetime decreased, dropping to 4 ms at the highest coverage, suggesting an increase in trapping of the conduction band electrons by IrO₂ particles on the surface of TiO₂. The apparent significance of this effect suggests that at least in this system, the back electron transfer pathway from TiO₂ to the sintered IrO₂ catalyst is at least as significant as back electron transfer to the oxidized dye. Thus, under illumination the open-circuit voltage of the cell can be described by^{5,20,25,28}

$$V_{oc} = \frac{RT}{\beta_e F} \ln \left(\frac{A\Phi}{n_e k_1 [\text{Ru}^{3+}] + n_e k_2 \Gamma_{Ir}} \right) \quad (1)$$

where n_e is the number density of conduction band electrons; k_1 and k_2 are the rate constants for back electron transfer to the oxidized dye and Ir(IV), respectively; Φ is the absorbed photon flux; A is the geometrical area of the photoanode; β_e is the reaction order of electrons, assumed to be unity; F , R , and T are the Faraday Constant, molar gas constant, and absolute temperature, respectively. Equation 1 shows that at low catalyst coverage, V_{oc} should be independent of Γ_{Ir} . We cannot unambiguously determine all the parameters in eq 1 from the data shown in Figure 5; in particular, n_e can vary with Γ_{Ir} . However, we note that the trend in Figure 5 is consistent with the equation. Further, using the typical value²⁹ of $\beta_e = 0.5$, we can derive approximate values of $2 \times 10^8 \text{ cm}^2 \text{ pmol}^{-1} \text{ s}^{-1}$ and $2 \times 10^8 \text{ s}^{-1}$ for the $n_e k_2$ product and $n_e k_1 [\text{Ru(III)}]$, respectively.

Equation 1 shows that at low catalyst coverage, the open-circuit voltage and thus photovoltage should be relatively constant. This is consistent with the trend in Figure 5, where the photovoltages measured with the 0.26 and 0.30 pmol Ir/cm² samples are the same within experimental error. From Figure 4, however, the photocurrent of the 0.26 pmol Ir/cm² sample is lower than that of the 0.30 pmol Ir/cm² sample, despite similar photovoltages. Likewise, the 0.50 pmol Ir/cm² samples have a photovoltage only about 20 mV higher than the 0.26 and 0.30 pmol Ir/cm² samples but have substantially higher photocurrent. We can explain these trends in photocurrent in terms of the relative coverage of the catalyst particles. Using an average of 130 Ir atoms per particle, the average TiO₂ surface area per particle can be calculated as shown in Table 1.

Table 1. Calculated TiO₂ Surface Area (Square Nanometers) per IrO₂ Particle and Area Sampled by Hole

loading of IrO ₂ (pmol/cm ²)	TiO ₂ surface area (nm ²) per IrO ₂ particle	area sampled by hole (nm ²)
0.26	81 000	790
0.30	72 000	750
0.50	44 000	720
0.84	26 000	610
1.79	12 000	530

As catalyst loading increases, the area per particle decreases and the probability of back electron transfer to IrO₂ increases. This process occurs in competition with lateral hole transfer and productive electron transfer from IrO₂ to Ru³⁺ as shown in Scheme 1. The hole moves across the TiO₂ surface via self-exchange between neighboring dye molecules (k_{diff}).³ Hanson et al. have measured a cross-surface diffusion constant for bis(2,2'-bipyridine)(4,4'-diphosphonato-2,2'-bipyridine)-ruthenium bromide of $13.3 \times 10^{-10} \text{ cm}^2/\text{s}$.³⁰ While the electron lifetimes in Figure 6 are obtained for unsensitized electrodes, they can be used to roughly estimate the area sampled by holes. This area can be estimated as the square of the hole diffusion

length, which is obtained as the product of the lifetime and the cross-surface diffusion coefficient. Table 1 shows that on the time scale of the electron lifetime, holes can sample only a small area before they recombine. If we approximate the particles within the porous TiO₂ film as spheres, the average TiO₂ particle has a surface area of $\sim 1200 \text{ nm}^2$. This means that holes are largely confined to the TiO₂ particle upon which they are generated. Unless that TiO₂ particle is also in contact with an IrO₂ particle, that hole will be lost to recombination. At low catalyst coverage, a relatively small fraction of the dye molecules can accept an electron from IrO₂ within the hole lifetime, resulting in efficient recombination via pathway k_1 and thus a low photocurrent. At higher catalyst loading, a greater fraction of holes can diffuse to the catalyst via pathway k_{diff} but back electron transfer to IrO₂ (pathway k_2) becomes kinetically important, as evidenced by the decrease in photovoltage and photocurrent for the 0.84 and 1.79 pmol/cm² samples. The optimum photovoltage and photocurrent for the 0.50 pmol/cm² sample thus represent a catalyst coverage that maximizes the rate of Ru(III) electron transfer from IrO₂ relative to the combined rates of the recombination pathways.

Amperometric Determination of O₂ Generated by the Photoanode. We previously determined that the current efficiency for oxygen evolution of ligand bound IrO_x catalysts was close to 100%.^{3,9} We used the same technique in this study, with two modifications to increase its accuracy and reproducibility. First, the active area of the Pt collector electrode was masked to 1.0 cm² by polyimide tape, which also served as a fixed-distance spacer. Second, the collection efficiency was determined by comparing the integrated current over 100 s as opposed to at a single time point.

Using a second platinum electrode, we determined that the collection efficiency for the collector electrode was 96%. For the calibration to be accurate, it was particularly important that the collector electrode be masked to a fixed area roughly consistent with the size of the TiO₂ electrodes. Despite vigorous purging with Ar, a slight background O₂ reduction current was observed. Over the time scale of the measurement, the decay of the background current was roughly linear. To correct for this background, the dark current just before illumination was measured and fitted linearly. The equation of this line was used to correct each data point from the collector electrode for reduction of background O₂ that was not generated by the photoanode.

A dye-sensitized 0.50 pmol Ir/cm² photoanode was used as the generator electrode (Figure 7). Under illumination for 100 s, the photoanode passed 54 mC of charge, while 50.4 mC of charge was passed at the collector electrode, giving a collection efficiency of 93%. By comparison to the collection efficiency of the Pt electrode, which is assumed to have 100% current efficiency for oxygen generation, we obtain a current efficiency of 98% for the WS-DSPEC photoanode.

CONCLUSION

Starting with citrate-capped IrO_x particles, IrO₂ nanoparticles were adsorbed and directly sintered to the TiO₂ film. These IrO₂ particles retain the small diameter of the precursor particles ($\sim 2 \text{ nm}$) and are in the rutile phase. On the basis of neutron activation analysis for Ir, only a very small portion of the electrode surface area is occupied by the catalyst, leaving most of the surface available for dye adsorption.

WS-DSPEC anodes containing these sintered nanoparticle catalysts initially produce relatively high photocurrents before

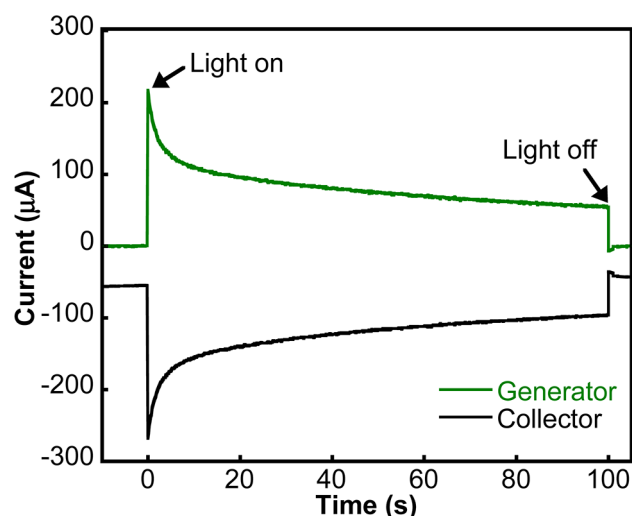


Figure 7. Generator–collector measurements on a dye-sensitized 0.50 pmol Ir/cm² sintered photoanode at +100 mV versus Ag/AgCl as generator. Planar platinum collector held at −650 mV versus Ag/AgCl.

rapidly polarizing. The photocurrent and photovoltage are not monotonic with catalyst loading, but reach a maximum with samples prepared from 100 μM citrate-capped IrO_x. Amperometric measurements of O₂ evolution determined that within experimental error the photocurrent efficiency for water oxidation is close to unity.

Photovoltage and EIS measurements provide some insight into the performance of the WS-DSPEC as a function of catalyst loading. EIS showed that the electron lifetime decreased with increasing catalyst loading, suggesting that conduction band electrons can recombine with IrO₂ particles on the surface of TiO₂. This introduces a hitherto unexplored loss pathway for WS-DSPECs. The significant effect on photovoltage introduced by different catalyst loadings suggests that electron transfer to the IrO₂ particles is a significant back electron-transfer pathway, in some cases more important than back electron transfer to the oxidized dye. Additional experiments are needed to understand if this is an important loss pathway in WS-PECs functionalized with other types of water oxidation catalysts. The rate of this process could be attenuated with a thin metal oxide layer between the catalyst and TiO₂,^{3,31} and further studies on this point are currently underway.

■ ASSOCIATED CONTENT

● Supporting Information

UV–vis spectrum of citrate-capped IrO_x; TEM images of citrate-capped IrO_x; FTIR spectra of citrate-capped IrO_x compared to sodium hydrogen sesquihydrate; XRD patterns of bare TiO₂ and catalyst functionalized electrodes; XPS of IrO₂ standard, citrate-capped IrO_x, and sintered catalyst; UV–vis spectra of unsensitized, catalyst-functionalized electrodes; photograph of the cell used for photoelectrochemical experiments; and energy level scheme for the WS-DSPEC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Prof. Ben Lear for assistance with FTIR measurements. This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Energy Biosciences, Department of Energy under Contract DE-FG02-07ER15911. J.R.S. was supported in part by the CarbonEARTH program, National Science Foundation GK-12 program, Grant DGE0947962. N.S.M., M.E.S., and N.M.V.-B. thank the National Science Foundation for support as graduate fellows under Grant DGE1255832. Instrumentation and facilities used in this project were supported by the Pennsylvania State University Materials Research Institute Nanofabrication Laboratory under National Science Foundation Cooperative Agreement ECS-0335765.

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