

¹ Heterogenized Iridium Water-Oxidation Catalyst from a Silatrane ² Precursor

³ Kelly L. Materna, Benjamin Rudshteyn, Bradley J. Brennan, Morgan H. Kane, Aaron J. Bloomfield, ⁴ Daria L. Huang, Dimitar Y. Shopov, Victor S. Batista,* Robert H. Crabtree,* and Gary W. Brudvig*

5 Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States

6 Yale Energy Sciences Institute, Yale University, West Haven, Connecticut 06516, United States

7 Supporting Information

ABSTRACT: A pentamethylcyclopentadienyl (Cp*) iridium water-8 oxidation precatalyst was modified to include a silatrane functional group 9 for covalent attachment to metal oxide semiconductor surfaces. The 10 heterogenized catalyst was found to perform electrochemically driven 11 water oxidation at an overpotential of 462 mV with a turnover number of 12 304 and turnover frequency of 0.035 s⁻¹ in a 0.1 M KNO₂ electrolyte at 13 pH 5.8. Computational modeling of experimental IR spectra suggests that 14 the catalyst retains its Cp* group during the first hour of catalysis and likely 15 remains monomeric. 16



17 KEYWORDS: alternative energy, electrocatalysis, iridium, metal oxide, silatrane, surface binding, water oxidation

¹⁸ Solar-to-fuel energy conversion is an outstanding challenge of ¹⁹ great current interest.¹ The intermittency problem for solar ²⁰ electricity generation by photovoltaics requires methods for ²¹ storage such as production of fuels¹⁻⁴ using photoelectrochem-²² ical cells (PECs).¹⁻⁷ Analogous to leaves in natural photosyn-²³ thesis,⁸ PECs capture sunlight and produce fuel by water ²⁴ splitting into O₂ and H₂. The generated H₂ can be directly used ²⁵ in fuel cells or converted into liquid fuels (e.g., methanol by ²⁶ reduction of CO₂) by efficient catalytic processes.

Some of the most active water-oxidation catalysts (WOCs) are iridium complexes, $^{9-14}$ although a variety of WOCs based on earth-abundant metals have been studied. 15,16 In particular, highly active WOCs synthesized from pentamethylcyclopentaidienyl (Cp*) iridium complexes have been reported. 9,13,17,18 Recently, we have been analyzing 1 (Chart 1) due to its high catalytic activity upon chemical or electrochemical activation. 9,19 The Cp* group of 1 is known to degrade into organic components such as acetic acid during activation. Cp*Ir-type precatalysts are much more likely to remain homogeneous

c1





when chelating ligands are bound to the iridium center. ³⁷ Without such ligands, however, the complexes can easily form ³⁸ heterogeneous IrO_2 nanoparticles that are also catalytically ³⁹ active.¹⁰ The Cp* degradation process of **1** yields a family of ⁴⁰ extremely active molecular catalysts. The presence of numerous ⁴¹ isomers, however, has made characterization of the catalyst ⁴² rather difficult.^{9,12} The identity of the homogeneous catalytic ⁴³ species derived from **1** is still unknown, although a proposed ⁴⁴ structure is a dimeric Ir(IV) species (**2**) shown in Chart 1.¹⁴ ⁴⁵ Catalyst **2** has also been bound to metal oxide surfaces, forming ⁴⁶ a heterogenized WOC, and remains catalytically active with a ⁴⁷ remarkable turnover frequency of 7.9 s⁻¹ when bound to nano-⁴⁸ ITO thin films.¹¹

Attaching the Cp*-bound catalyst precursors to the metal ⁵⁰ oxide surface is expected to isolate the precatalyst complexes. If ⁵¹ Cp* loss is a bimolecular reaction, surface binding will slow the ⁵² Cp* oxidation reactions and enable the precatalysts to remain ⁵³ active for water oxidation. Binding the precatalyst rigidly on the ⁵⁴ metal oxide surface should also limit the possibility of dimer ⁵⁵ formation.^{20,21} A similar strategy was applied by Lin and co-⁵⁶ workers, who supported similar Cp*Ir precatalysts in a ⁵⁷ molecular organic framework (MOF). When treated with ⁵⁸ chemical oxidants, the Cp* ring was degraded to yield active ⁵⁹ monomeric WOCs.²⁰ Here, we utilize an electrochemical ⁶⁰ activation approach which may provide greater control of the ⁶¹

Received: April 18, 2016 Revised: July 4, 2016 s1

62 system preparation and thus more insight into potential 63 mechanisms.

64 Complex **3** (Scheme 1) was designed to enable formation of 65 a heterogenized water-oxidation catalyst upon binding to metal

Scheme 1. Complex 3 (left) Containing a Silatrane Functional Group and the Heterogenized WOC upon Binding to Nano-ITO or TiO_2 (right)



66 oxide surfaces such as TiO2 or nanoporous indium tin oxide 67 (nano-ITO). Specifically, the silatrane functional group in 3 was 68 designed for surface binding. These anchoring groups are 69 known to be relatively unreactive during synthetic steps, 70 although they are still capable of hydrolyzing on metal oxide 71 surfaces to form strong, water-stable, siloxane surface bonds 72 that are stable under acidic, neutral, and alkaline conditions.² 73 In contrast, other surface-binding groups such as carboxylates, 74 phosphonates, or hydroxamates make the synthesis of inorganic 75 complexes more difficult because they have a tendency to bind 76 to metal centers and exchange with the ligands more easily than 77 silatranes.^{23–26} In addition, silatranes form stable bonds with 78 metal oxide surfaces over a pH range much more extended than 79 that of other anchoring groups.²³⁻²⁶ The phenylene spacer 80 between the silatrane and pyridine alkoxide ring was 81 implemented to provide a rigid, anchored molecule that is 82 expected to have limited interaction with other molecules on 83 the surface.

⁸⁴ Our characterization of the surface-bound species was based ⁸⁵ on a combination of spectroscopic, electrochemical, and ⁸⁶ computational analyses, including a comparison of the ⁸⁷ spectroscopy of **3** in solution to the corresponding spectra of surface-bound **3**. The heterogenized system $(3-\text{TiO}_2 \text{ or } 3\text{-nano-} 88$ ITO) was then successfully tested for water-oxidation catalysis. 89 The system was studied electrochemically under controlled 90 conditions, and the surface was analyzed using infrared (IR) 91 spectroscopy, cyclic voltammetry (CV), energy dispersive X-ray 92 (EDX) spectroscopy, and UV-visible spectroscopy to 93 determine if the structure changes under an applied bias. IR 94 spectra were compared to density functional theory (DFT) 95 calculations. The experiments and models were designed to 96 provide evidence for the catalytic activity and insights on the 97 mechanism. Additionally, the system is a potential catalytic 98 component of a PEC for solar fuel production.

Complex 3 was synthesized by a standard method that 100 mirrors the synthesis of 1: reaction of $(Cp*IrCl_2)_2$ with the 101 pyridine alkoxide ligand (7) and NaHCO₃ in acetone (see the 102 Supporting Information for experimental details).¹⁹ Complex 3 103 was isolated and purified by dissolving the crude product in 104 dichloromethane and layering with n-octane for one week, 105 which resulted in a red-orange precipitate in 93% yield. The 106 NMR spectrum of the complex showed all of the signals 107 expected for the proposed structure, notably a singlet at 1.66 108 ppm for the Cp* and a pair of triplets at 2.99 and 3.80 ppm for 109 the silatrane group. Mass spectrometry data also support the 110 proposed structure with m/z of 791 for 3 and m/z of 756 for 3 111 without a bound chloride. UV-visible spectroscopic measure- 112 ments show two bands at 229 and 280-320 nm, and IR 113 spectroscopic data verify the presence of the carbonyl, amide, 114 silatrane cage, Cp*, and pyridine alkoxide components in the 115 structure.

To facilitate binding to the metal oxide surface, **3** was ¹¹⁷ dissolved in acetonitrile (~30 μ M). The nano-ITO or TiO₂ ¹¹⁸ electrode was soaked in the solution and then heated overnight ¹¹⁹ at 70 °C in the dark under a nitrogen atmosphere. ^{22,24,27} The ¹²⁰ nano-ITO electrode itself, consisting of nanoporous indium tin ¹²¹ oxide deposited onto an FTO-coated glass slide, was prepared ¹²² by previously reported methods. ^{21,28}

The absorption spectra of both 3-nano-ITO and 3-TiO₂ were 124 dominated by the metal oxide absorption (Figures S1 and S2), 125 and no precipitation was observed during sensitization. 126 Therefore, the surface coverage was determined by calculating 127 the difference between the initial amount of **3** in the 128 sensitization solution and the final amount after sensitization 129 of nano-ITO or TiO₂, A surface coverage of 40–60 nmol cm⁻² 130 was obtained after 5 h on TiO₂ and nano-ITO, which is a 131 typical range for these surfaces (Supporting Information).^{21,22} 132 Complex **3** was bound to nano-ITO as **3**-nano-ITO to study 133



Figure 1. ATR-FTIR spectra of 3 and 3-TiO₂.



Figure 2. Experimental spectrum of 3 (blue) and calculated spectrum of 3 considering water hydrogen bonding to the complex (red).

¹³⁴ electrochemical and catalytic properties of the heterogenized ¹³⁵ system. In addition, it was bound to TiO_2 as 3- TiO_2 for ¹³⁶ characterization of the covalently bound complex using ¹³⁷ attenuated total reflectance (ATR)-FTIR spectroscopy.

The proposed structure **3**-TiO₂ or **3**-nano-ITO (Scheme 1) follows from the characterization data.²³ Although ATR-FTIR spectroscopy has been previously used to study porphyrins on the metal oxide surfaces,²³ nano-ITO and **3**-nano-ITO surfaces are usuitable for ATR-FTIR spectroscopy due to interference from surface plasmon effects. Scanning electron microscopy (SEM)-EDX measurements show the presence of iridium on the metal oxide surfaces (Figures S6 and S7).

Due to overpowering absorption from the metal oxide, UV-146 147 visible spectroscopy could not be used for characterization of 3-148 TiO₂ or 3-nano-ITO (Figures S1 and S2). However, ATR-149 FTIR spectroscopy was available for 3-TiO₂ with a hydroxy-150 lated surface analogous to 3-nano-ITO. We found that the 151 ATR-FTIR spectra of 3 and 3-TiO₂ (Figure 1) are very similar. 152 The silatrane cage ATR-FTIR bands of 3 at 1452 cm⁻¹ for 153 $\delta(CH_2)$ and 1170 cm⁻¹ for $\nu(C-O)$ disappear upon formation 154 of 3-TiO₂ by surface binding, as previously observed for other 155 systems, including porphyrin-silatranes bound to metal oxide 156 surfaces.²³ The functional groups C=O (1689 cm⁻¹ stretch), 157 N-H (1515 cm⁻¹ bend), C=C (pyridine alkoxide, 1590 cm⁻¹ 158 stretch), C-H (alkoxide methyls, 2856, 2916, and 2960 cm⁻¹) 159 and C-H (Cp* methyls, 2856 and 2960 cm⁻¹) bands were 160 identified in the ATR-FTIR of 3 and 3-TiO₂ and appear close 161 to the theoretically determined values (within 25 cm^{-1}), thus 162 supporting our assignments (Table S1). The complex seems to 163 remain intact upon binding. In particular, the IR data suggest 164 that the Cp* ring remains bound to iridium upon surface 165 binding and that the amide bond is still present. The IR 166 assignments were identified by comparing ATR-FTIR spectra 167 of 3 and 3-TiO₂ to Na[Cl₄Ir(2-(2'-pyridyl)-2-propanolate)], 168 Cp*Ir(2-(2'-pyridyl)-2-propanolate)Cl, 7 (Scheme S1), 7-169 TiO₂, p-tolyl silatrane, and p-tolyl-silatrane-TiO₂ (Figures 170 S13-S19).

¹⁷¹ Our spectroscopic assignments are consistent with the DFT ¹⁷² IR spectra (Figure 2) obtained from B3LYP/(LANL2DZ/6-¹⁷³ 311G(d,p)) geometries (see the Supporting Information for ¹⁷⁴ theoretical details). The geometry of **3**, including three water ¹⁷⁵ molecules (Chart 2), was found to be in much better agreement ¹⁷⁶ with the experimental IR spectra (Figure 2) than model ¹⁷⁷ structures without hydrogen-bonding waters (Figures S11 and ¹⁷⁸ S12).

The DFT-IR spectrum of 3-TiO₂ was computed for a model structure built by attaching 3 in the bidentate siloxane binding mode (Chart 2 and Figure S12), which was previously determined to be the most stable attachment mode to the Chart 2. Optimized Structures of 3 and 3-TiO_2 with Water Molecules Hydrogen Bonded to the C=O, N-H, and Pyridine Alkoxide O^{*a*}



^{*a*}Left: Optimized structure of **3**. Right: 3-TiO_2 in a bidentate mode. Atom labels: carbon (dark grey), hydrogen (light gray, small spheres), oxygen (red), nitrogen (small blue spheres), iridium (large blue spheres), and titanium (grey large spheres). Hydrogen bonds are indicated by dashed lines.

[101] surfaces of TiO₂ anatase.²⁹ The model includes 6 TiO₂ 183 units capped with hydroxides to ensure realistic modeling 184 consistent with neutral pH conditions. The calculated ATR- 185 FTIR spectrum of 3-TiO₂ shows good agreement with 186 experimental bands in the 1000–1800 cm⁻¹ region, suggesting 187 that the monomeric catalysts are not significantly interacting 188 with each other. Deviations in the 2800–3100 cm⁻¹ region 189 suggest some level of inhomogeneity not captured by a single 190 configuration (Figures S11 and S12).

The electrochemical analysis of the 3-nano-ITO system in 192 aqueous 0.1 M KNO₃ at pH 5.8 shows a redox couple at 0.9 V 193 vs NHE (Figure 3a) assigned to the Ir(III/IV) couple. A similar 194 f3 couple is seen for 2 and 2-nano-ITO.^{9,18} The CV of 3 in 0.1 M 195 tetrabutylammonium hexafluorophosphate in acetonitrile also 196 shows an Ir(III/IV) redox couple at 0.93 V vs NHE and what 197 may be an Ir(IV/V) redox couple at 1.35 V vs NHE (Figure 198 S20). Figure 3b shows a CV of 3-nano-ITO with a catalytic 199 wave, suggesting that water-oxidation catalysis is occurring 200 when higher potentials are reached. When the scan rates of the 201 CVs of 3-nano-ITO were varied, a linear dependence of current 202 versus scan rate was found, indicative of a surface-bound species 203 (Figure S21). Spectroelectrochemical experiments of 3-nano-204 ITO were also performed at 0, 1.35, and 1.55 V vs NHE 205

f1

 f_2



Figure 3. (a) Cyclic voltammogram of 3-nano-ITO in 0.1 M KNO₃ at pH 5.8 with a scan rate of 50 mV/s. The high capacitive current is due to the nano-ITO electrode. (b) Cyclic voltammogram under the same conditions, showing the catalytic water-oxidation wave at 1.35 V vs NHE for 3-nano-ITO (red). A blank nano-ITO electrode shows minimal current flow (black).



Figure 4. (a) O_2 evolved when a bias of 1.35 V vs NHE was applied from 10 to 40 min to the electrochemical cell containing 3-nano-ITO (solid line). (b) O_2 evolved when a bias of 1.35 V vs NHE was applied after 10 min to the electrochemical cell containing 3-nano-ITO for 4.2 h (solid line). The O_2 produced experimentally does not increase past 4.2 h. Theoretical O_2 evolution is also shown and was calculated based on the amount of charge passed during the electrolysis (dashed lines).

²⁰⁶ (Figure S22), although no changes in the UV–visible spectra ²⁰⁷ were observed. **2** is known to absorb at around 600 nm and has ²⁰⁸ a deep blue color when the active catalyst forms from **1**, ²⁰⁹ indicative of a μ -oxo dimer.⁹ However, **3**-nano-ITO does not ²¹⁰ form a blue species under these conditions, suggesting that the ²¹¹ oxidized complex is structurally distinct from **2**.

Heterogenized 3-nano-ITO was also studied electrochemi-212 213 cally for water-oxidation catalysis. An O₂ assay was carried out using a Clark electrode. Data for 3-nano-ITO were collected 214 215 under electrochemical conditions by first collecting a baseline 216 reading for the first 10 min of each experiment, followed by a 30 min run of electrolysis at 1.35 V vs NHE, and ending with a 217 10 min period with no applied bias (Figure 4a). Oxygen was 218 produced immediately when 1.35 V was applied, and Faradaic 219 yields averaged 92% over the time frame studied (Figure 4a). 220 The 3-nano-ITO catalyst has a 462 mV overpotential at pH 5.8, 221 which is defined by the minimum applied potential required to 222 223 measure O₂. An average turnover frequency of 0.035 \pm 0.015 s⁻¹ for 3-nano-ITO was observed. A nano-ITO blank electrode 224 225 did not evolve O2 under the same conditions, suggesting that 226 the O₂ produced in Figure 4a is from the iridium catalyst 227 (Figure S26). Additionally, nitrate has been suggested to participate in water-oxidation catalytic mechanisms when 228 present in the chemical oxidant, cerium ammonium nitrate.^{30,31} 229 To make sure that the catalyst could function without nitrate, 230 231 3-nano-ITO was also tested for electrochemically driven WO 232 catalysis in sodium triflate, which was found to produce O₂ 233 upon electrolysis (Figures S27 and S28).

Complex 1 was found to take up to 36 h to form the active 234 dimeric catalyst 2 electrochemically when a highly oxidizing 235 bias of 1.6 V vs NHE is applied during electrolysis due to the 236 required detachment and degradation of the Cp* ring.⁹ Because 237 3-nano-ITO evolves O2 immediately with no lag phase when a 238 bias is applied and with high initial Faradaic efficiency, we 239 believe that Cp* may well remain bound to the complex during 240 catalysis. In fact, a prior computational study suggested that 241 there is a low energy pathway for water-oxidation catalysis for a 242 related Cp*Ir catalyst. Thus, Cp* loss may not be required for 243 water oxidation.¹³ The nano-ITO surface prohibits diffusion of 244 the covalently bound 3 in the electrolyte, and the Ir centers 245 may be too far apart on the surface or in incorrect orientations 246 to interact, which could result in Cp* remaining intact. The 247 electrochemical conditions for electrocatalysis by 3-nano-ITO 248 are also significantly milder than those used for electrolysis of 1, 249 which could also contribute to the retention of the Cp* ring. 250

To see if Cp* indeed remains bound to Ir during water- $_{251}$ oxidation catalysis, a series of electrolyses at 1.35 V vs NHE $_{252}$ using 3-TiO₂ as the working electrode were performed for 0, 1, $_{253}$ 6, and 20 h. ATR-FTIR spectra of 3-TiO₂ post-electrolysis were $_{254}$ obtained. During the 1 h electrolysis, chosen to mimic the time $_{255}$ frame of the O₂ measurement in Figure 4a, no change in the $_{256}$ ATR-FTIR spectrum of 3-TiO₂ was observed (Figure S18), $_{257}$ suggesting that Cp* indeed remained bound to the iridium $_{258}$ during the first hour of catalysis. Upon prolonging the $_{259}$ electrolysis over 6 h, the ATR-FTIR spectrum of the modified $_{260}$ 3'-TiO₂ showed a gradual disappearance of the C–H stretching 261



Figure 5. ATR-FTIR spectra of 3-TiO₂ before (blue) and 3'-TiO₂ after a 6 h electrolysis (red) at 1.35 V vs NHE.

262 frequencies of the Cp* methyl groups at 2856 and 2960 cm⁻¹, 263 suggesting the oxidation of the Cp* ring and a shift in the N–H 264 and C=C stretching frequencies due to a change in the iridium 265 coordination sphere (Figure 5). We now represent 3'-TiO₂ as 266 the structurally modified surface complex upon Cp* oxidation; 267 however, the exact structure remains unknown. After 20 hours 268 of electrolysis, only the alkyl C–H stretching bands assigned to 269 the pyridine alkoxide ligand and the C=O stretch remain, so 270 Cp* is likely removed at this point (Figure S19).

To understand how the Cp* loss affects catalysis, a long-term 272 electrolysis was carried out on 3-nano-ITO with O_2 evolution 273 measured as before (Figure 4b). After 4.2 h of electrolysis, the 274 catalytic activity reached a maximum after 304 turnovers. 275 Interestingly, the Faradaic yield is 82% up to 1.4 h but slowly 276 decreases to 44% at 4.2 h. A chronoamperogram obtained 277 during the electrolysis initially shows a stable current and then a 278 rise in current after 1.4 h (Figure 6). Based on the ATR-FTIR



Figure 6. Chronoamperogram of 3-nano-ITO over 4.2 h when a 1.35 V bias vs NHE is applied.

279 electrolysis measurements, both the increase in current flow 280 and the reduced Faradaic yield are most likely due to Cp^* 281 oxidation, which deactivates 3-nano-ITO during water-282 oxidation catalysis. Oxidation of the Cp^* is known to form 283 organic acids such as acetic and formic acid as well as carbon 284 dioxide, which could account for some of the nonproductive 285 oxidizing events.¹²

Although Cp* oxidation seems like the most likely culprit for the lower Faradaic yields, we cannot exclude other nonproductive oxidation events that could be occurring in our system. When the silatrane cage binds to the metal oxide surface, forming the proposed structure in Scheme 1, the riethanolamine portion of the silatrane cage also remains bound to the metal oxide surface as part of the surface binding process and thus may contribute to some of the nonproductive 293 oxidation events. To probe this possibility, electrodes 294 containing tolylsilatrane bound to nano-ITO, which should 295 only show oxidation of triethanolamine, were prepared, and CV 296 measurements were performed (Figure S24). Indeed, one 297 irreversible oxidation event is observed for the first CV of the 298 tolylsilatrane-nano-ITO electrodes, suggesting that oxidation of 299 triethanolamine is possible. Upon running a second CV trace, 300 the original signal disappears, which is indicative that the 301 oxidation event is complete. Additionally, nano-ITO electrodes 302 that have been sensitized with pure triethanolamine also follow 303 the same CV trends as the tolylsilatrane-nano-ITO electrodes 304 (Figure S25). Finally, formation of H_2O_2 is another possible 305 oxidation event that could contribute to the lower Faradaic 306 vields.32 307

Prior work has demonstrated that 1 is not an active water- 308 oxidation catalyst under electrochemical conditions.⁹ For 1 to 309 become an active water-oxidation catalyst in a homogeneous 310 solution, Cp* degradation and iridium dimerization must occur, 311 whereas 3-nano-ITO appears to be active while retaining its 312 Cp* group and remaining mononuclear. The differences 313 between the two systems may well account for their different 314 reactivity. Importantly, 1 was studied under homogeneous 315 conditions where the molecules are able to diffuse in solution 316 and mutually interact. Previous studies have suggested that 317 Cp*Ir complexes are able to form high valent Ir(V) = O species 318 under oxidizing conditions, which are then capable of 319 preferential reaction with organic substrates over reaction 320 with water.^{33,34} Thus, it is possible that 1 may be capable of 321 performing bimolecular Cp* oxidation by reaction of one 322 Ir(V) = O group with another Cp*Ir species in solution. If this 323 process is dominant, then the lack of water-oxidation catalysis 324 in homogeneous solution can be explained. As another 325 possibility, 3-nano-ITO is a heterogenized system where 326 there can be no diffusion of 3, and binding to the surface 327 may impose stereoelectronic limitations on the way the 328 molecular units can interact on the nano-ITO surface. Because 329 the catalysts on the nano-ITO surface are less likely to interact, 330 bimolecular Cp* degradation is less likely to occur and, thus, 331 water-oxidation catalysis dominates. 332

Lin and co-workers have previously demonstrated that 333 mononuclear iridium WOCs in MOFs are active when Cp^{*} 334 is removed using chemical oxidants.²⁰ We importantly note, 335 however, that in a MOF with strong chemical oxidants along 336 with their detritus upon Cp^{*} oxidation, the environment is not 337 comparable to that of **3**-nano-ITO, which uses mild electro- 338 chemical conditions. However, their study does suggest that 339 iridium dimerization is not required for catalytic activity, which 340

341 also supports our hypothesis that 3-nano-ITO could be an 342 active monomeric water-oxidation catalyst without loss of Cp* 343 or dimerization. For 3-nano-ITO to remain an active WOC 344 after Cp* oxidation, 3-nano-ITO may need to dimerize on the 345 surface to stabilize the iridium center and form a species similar 346 to dimer-2 when electrochemical conditions are used. However, 347 the iridium centers may be too far apart on the nano-ITO 348 surface, causing loss of catalytic performance. The CV of the 349 used electrolyte post-electrolysis at 1.35 V vs NHE for 20 h of 350 3-nano-ITO using a blank nano-ITO working electrode is 351 identical to the CV using fresh electrolyte, which suggests that $_{352}$ 3 has not leached into the electrolyte from the TiO₂ surface due 353 to the strong siloxane surface bounds (Figure S23).²² Iridium 354 was detected post-electrolysis of 3-TiO₂ by SEM-EDX measurements of 3-TiO₂ (Figure S8). 355

Electrochemical catalytic water-oxidation measurements of 3-356 357 nano-ITO have suggested that Cp*Ir complexes are able to function as water-oxidation catalysts by binding to metal oxide 358 359 surfaces without Cp* degradation as indicated by experimental 360 and theoretical IR spectra. The surface-bound species could be monomeric because 3 is isolated on a surface and the Cp* 361 remains bound to the iridium center under mild oxidizing 362 363 conditions. Thus, the 3-nano-ITO system is likely to operate differently from 2, giving new insights on how Cp*Ir complexes 364 can behave on metal oxide surfaces as monomeric WOCs. 365

We conclude that covalent attachment of the Cp*Ir system 366 367 to metal oxide surfaces in a monomeric form suppresses degradation and allows for probing catalytic activity. Degrada-368 369 tion of Cp* in the 3-nano-ITO system, however, forms an 370 inactive surface-bound catalyst. Inactivation is likely due to the isolation of the monomers on the surface that might be too far 371 372 apart to form a more active dimeric catalyst upon Cp* degradation. Our findings thus highlight the importance of 373 using the dinuclear form of the iridium catalyst for rapid water-374 oxidation catalysis. These results are consistent with the 375 376 observation that the monomeric catalyst, 3-nano-ITO, exhibits 377 rates of water-oxidation catalysis much slower (~200 times 378 slower) than those of the previously studied solution phase 379 dimeric catalyst 2.9 Routes to make 3-nano-ITO a more facile 380 WOC are currently being explored, including its use in PECs.

381 **ASSOCIATED CONTENT**

382 **Supporting Information**

383 The Supporting Information is available free of charge on the 384 ACS Publications website at DOI: 10.1021/acscatal.6b01101.

Experimental and theoretical methods, UV-visible data, EDX data, ATR-FTIR experimental and theoretical data, geometry of **3** without water molecules, additional references, electrochemical data, O_2 assay data, and theoretical coordinates of **3** (with and without water molecules) and **3**-TiO₂ (PDF)

391 **AUTHOR INFORMATION**

392 Corresponding Authors

- 393 *E-mail: victor.batista@yale.edu.
- 394 *E-mail: robert.crabtree@yale.edu.
- 395 *E-mail: gary.brudvig@yale.edu.

396 Present Address

397 B.J.B.: California Institute of Technology, Pasadena, California 398 91125, United States.

399 Notes

400 The authors declare no competing financial interest.

415

ACKNOWLEDGMENTS

This material is based upon work supported as part of the 402 Argonne-Northwestern Solar Energy Research (ANSER) 403 Center, an Energy Frontier Research Center funded by the 404 U.S. Department of Energy, Office of Science, Office of Basic 405 Energy Sciences, under Award Number DE-SC0001059. 406 Additional funding was provided by a generous donation 407 from the TomKat Charitable Trust. V.S.B. acknowledges high 408 performance computing time from NERSC and the high 409 performance computing facilities at Yale and Shanghai Jiao 410 Tong University. B.R. acknowledges support from the National 411 Science Foundation Graduate Research Fellowship under 412 Grant DGE-1122492. We thank Subhajyoti Chaudhuri and 413 the group of Charles A. Schmuttenmaer for helpful discussions. 414

REFERENCES

(1) Young, K. J.; Martini, L. A.; Milot, R. L.; Snoeberger, R. C., III; 416 Batista, V. S.; Schmuttenmaer, C. A.; Crabtree, R. H.; Brudvig, G. W. 417 *Coord. Chem. Rev.* **2012**, 256, 2503–2520. 418

(2) Gust, D.; Moore, T. A.; Moore, A. L. Acc. Chem. Res. 2009, 42, 419 1890–1898. 420

(3) Berardi, S.; Drouet, S.; Francas, L.; Gimbert-Surinach, C.; 421 Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A. *Chem. Soc. Rev.* 422 **2014**, 43, 7501–7519. 423

(4) Ganesh, I. Renewable Sustainable Energy Rev. 2015, 44, 904-932. 424

(5) Wang, L.; Mirmohades, M.; Brown, A.; Duan, L.; Li, F.; Daniel, 425
 Q.; Lomoth, R.; Sun, L.; Hammarström, L. *Inorg. Chem.* 2015, 54, 426
 2742–2751.

(6) Lapides, A. M.; Sherman, B. D.; Brennaman, M. K.; Dares, C. J.; 428 Skinner, K. R.; Templeton, J. L.; Meyer, T. J. *Chem. Sci.* **2015**, *6*, 429 6398–6406. 430

(7) Gao, Y.; Zhang, L.; Ding, X.; Sun, L. Phys. Chem. Chem. Phys. 431 2014, 16, 12008–12013. 432

(8) Vinyard, D. J.; Ananyev, G. M.; Dismukes, G. C. Annu. Rev. 433 Biochem. 2013, 82, 577–606. 434

(9) Thomsen, J. M.; Sheehan, S. W.; Hashmi, S. M.; Campos, J.; 435
 Hintermair, U.; Crabtree, R. H.; Brudvig, G. W. J. Am. Chem. Soc. 436
 2014, 136, 13826–13834.

(10) Thomsen, J. M.; Huang, D. L.; Crabtree, R. H.; Brudvig, G. W. 438 Dalton Trans. 2015, 44, 12452–12472. 439

(11) Sheehan, S. W.; Thomsen, J. M.; Hintermair, U.; Crabtree, R. 440 H.; Brudvig, G. W.; Schmuttenmaer, C. A. Nat. Commun. 2015, 6, 441 6469–6477. 442

(12) Savini, A.; Belanzoni, P.; Bellachioma, G.; Zuccaccia, C.; 443 Zuccaccia, D.; Macchioni, A. *Green Chem.* **2011**, *13*, 3360–3374. 444

- (13) Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; 445 Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2009**, 446 131, 8730–8731. 447
- (14) Yang, K. R.; Matula, A. J.; Kwon, G.; Hong, J.; Sheehan, S. W.; 448 Thomsen, J. M.; Brudvig, G. W.; Tiede, D. M.; Chen, L. X.; Batista, V. 449 S.; Crabtree, R. H. J. Am. Chem. Soc. **2016**, 138, 5511–5514.

(15) Khan, S.; Yang, K. R.; Ertem, M. Z.; Batista, V. S.; Brudvig, G. 451 W. ACS Catal. **2015**, *5*, 7104–7113. 452

(16) Rivalta, I.; Yang, K. R.; Brudvig, G. W.; Batista, V. S. ACS Catal. 453 2015, 5, 2384–2390. 454

(17) Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, 455 G. W.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. 456 J. Am. Chem. Soc. **2010**, 132, 16017–16029. 457

(18) Li, W.; Sheehan, S. W.; He, D.; He, Y.; Yao, X.; Grimm, R. L.; 458 Brudvig, G. W.; Wang, D. Angew. Chem., Int. Ed. **2015**, 54, 11428-459 11432. 460

(19) Schley, N. D.; Blakemore, J. D.; Subbaiyan, N. K.; Incarvito, C. 461 D.; D'Souza, F.; Crabtree, R. H.; Brudvig, G. W. J. Am. Chem. Soc. 462 **2011**, 133, 10473–10481. 463

(20) Wang, C.; Wang, J. L.; Lin, W. J. Am. Chem. Soc. 2012, 134, 464 19895–19908. 465

- 466 (21) Chen, Z.; Concepcion, J. J.; Hull, J. F.; Hoertz, P. G.; Meyer, T.
 467 J. Dalton Trans. 2010, 39, 6950–6952.
- 468 (22) Materna, K. L.; Brennan, B. J.; Brudvig, G. W. Dalton Trans. 469 **2015**, 44, 20312–20315.
- 470 (23) Brennan, B. J.; Llansola Portoles, M. J.; Liddell, P. A.; Moore, T.

471 A.; Moore, A. L.; Gust, D. Phys. Chem. Chem. Phys. 2013, 15, 16605– 472 16614.

473 (24) Brennan, B. J.; Keirstead, A. E.; Liddell, P. A.; Vail, S. A.; Moore,

474 T. A.; Moore, A. L.; Gust, D. Nanotechnology **2009**, 20, 505203–475 505212.

- 476 (25) Mollmann, U.; Heinisch, L.; Bauernfeind, A.; Kohler, T.; Ankel-477 Fuchs, D. *BioMetals* **2009**, *22*, 615–624.
- 478 (26) Brewster, T. P.; Konezny, S. J.; Sheehan, S. W.; Martini, L. A.;
 479 Schmuttenmaer, C. A.; Batista, V. S.; Crabtree, R. H. *Inorg. Chem.*480 2013, 52, 6752–6764.

481 (27) Brennan, B. J.; Gust, D.; Brudvig, G. W. Tetrahedron Lett. 2014, 482 55, 1062–1064.

483 (28) Hoertz, P. G.; Chen, Z.; Kent, C. A.; Meyer, T. J. *Inorg. Chem.* 484 **2010**, 49, 8179–8181.

485 (29) Iguchi, N.; Cady, C.; Snoeberger, R. C., III; Hunter, B. M.;
486 Sproviero, E. M.; Schmuttenmaer, C. A.; Crabtree, R. H.; Brudvig, G.
487 W.; Batista, V. S. *Proc. SPIE* 2008, 7034, C1–C8.

488 (30) Stull, J. A.; Britt, R. D.; McHale, J. L.; Knorr, F. J.; Lymar, S. V.;
489 Hurst, J. K. J. Am. Chem. Soc. 2012, 134, 19973–19976.

(21) L: D.7. L: X.C. C: 1.1. D.F.M.F. L.L.

490 (31) Liao, R.-Z.; Li, X.-C.; Siegbahn, P. E. M. Eur. J. Inorg. Chem.
491 2014, 2014, 728-741.

492 (32) Izgorodin, A.; Izgorodina, E.; MacFarlane, D. R. *Energy Environ.*493 Sci. 2012, 5, 9496–9501.

494 (33) Zhou, M.; Schley, N. D.; Crabtree, R. H. J. Am. Chem. Soc. 2010, 495 132, 12550–12551.

496 (34) Zhou, M.; Balcells, D.; Parent, A. R.; Crabtree, R. H.; Eisenstein, 497 O. ACS Catal. **2012**, *2*, 208–218.