Heterogenized Iridium Water-Oxidation Catalyst from a Silatrane Precursor

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ABSTRACT: A pentamethylcyclopentadienyl (Cp*) iridium water-oxidation precatalyst wasmodified to include a silatrane functional group for covalent attachment to metal oxide semiconductor surfaces. The heterogenized catalyst was found to perform electrochemically driven water oxidation at an overpotential of 462 mV with a turnover number of 304 and turnover frequency of 0.035 s⁻¹ in a 0.1 M KNO₃ electrolyte at pH 5.8. Computational modeling of experimental IR spectra suggests that the catalyst retains its Cp* group during the first hour of catalysis and likely remains monomeric.

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

Solar-to-fuel energy conversion is an outstanding challenge of great current interest. The intermittency problem for solar electricity generation by photovoltaics requires methods for storage such as production of fuels using photoelectrochemical cells (PECs). Analogous to leaves in natural photosynthesis, PECs capture sunlight and produce fuel by water splitting into O₂ and H₂. The generated H₂ can be directly used in fuel cells or converted into liquid fuels (e.g., methanol by reduction of CO₂) by efficient catalytic processes.

Some of the most active water-oxidation catalysts (WOCs) are iridium complexes, although a variety of WOCs based on earth-abundant metals have been studied. In particular, highly active WOCs synthesized from pentamethylcyclopentadienyl (Cp*) iridium complexes have been reported. Recently, we have been analyzing 1 (Chart 1) due to its high catalytic activity upon chemical or electrochemical activation. 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 when chelating ligands are bound to the iridium center. Without such ligands, however, the complexes can easily form heterogeneous IrO₂ nanoparticles that are also catalytically active. The Cp* degradation process of 1 yields a family of extremely active molecular catalysts. The presence of numerous isomers, however, has made characterization of the catalyst rather difficult. The identity of the homogeneous catalytic species derived from 1 is still unknown, although a proposed structure is a dimeric Ir(IV) species shown in Chart 1. Catalyst 2 has also been bound to metal oxide surfaces, forming a heterogenized WOC, and remains catalytically active with a remarkable turnover frequency of 7.9 s⁻¹ when bound to nanITO thin films. Here, we utilize an electrochemical activation approach which may provide greater control of the

Chart 1. Precatalyst 1 and Hypothesized Active Catalyst 2

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Complex 3 (Scheme 1) was designed to enable formation of a heterogenized water-oxidation catalyst upon binding to metal oxide surfaces such as TiO$_2$ or nanoporous indium tin oxide (nano-ITO). Specifically, the silatrane functional group in 3 was designed for surface binding. These anchoring groups are known to be relatively unreactive during synthetic steps, although they are still capable of hydrolyzing on metal oxide surfaces to form strong, water-stable, siloxane surface bonds that are stable under acidic, neutral, and alkaline conditions. Designed for surface binding, these anchoring groups are expected to have limited interaction with other molecules on the surface.

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

Complex 3 was synthesized by a standard method that mirrors the synthesis of 1: reaction of (Cp*$^2$IrCl$_2$)$_2$ with the pyridine alkoxide ligand (7) and NaNHCO$_3$ in acetone (see the Supporting Information for experimental details). Complex 3 was isolated and purified by dissolving the crude product in dichloromethane and layering with n-octane for one week, which resulted in a red-orange precipitate in 93% yield. The NMR spectrum of the complex showed all of the signals expected for the proposed structure, notably a singlet at 1.66 ppm for the Cp* and a pair of triplets at 2.99 and 3.80 ppm for the silatrane group. Mass spectrometry data also support the proposed structure with m/z of 791 for 3 and m/z of 756 for 3 without a bound chloride. UV-visible spectroscopic measurements show two bands at 229 and 280–320 nm, and IR spectroscopic data verify the presence of the carbonyl, amide, silatrane cage, Cp*, and pyridine alkoxide components in the structure.

To facilitate binding to the metal oxide surface, 3 was dissolved in acetonitrile (~30 μM). The nano-ITO or TiO$_2$ electrode was soaked in the solution and then heated overnight at 70 °C in the dark under a nitrogen atmosphere. The nano-ITO electrode itself, consisting of nanoporous indium tin oxide deposited onto an FTO-coated glass slide, was prepared by previously reported methods. The absorption spectra of both 3-nano-ITO and 3-TiO$_2$ were dominated by the metal oxide absorption (Figures S1 and S2), and no precipitation was observed during sensitization. Therefore, the surface coverage was determined by calculating the difference between the initial amount of 3 in the sensitization solution and the final amount after sensitization of nano-ITO or TiO$_2$. A surface coverage of 40–60 nmol cm$^{-2}$ was obtained after 5 h on TiO$_2$ and nano-ITO, which is a typical range for these surfaces (Supporting Information).

Complex 3 was bound to nano-ITO as 3-nano-ITO to study...
electrochemical and catalytic properties of the heterogenized system. In addition, it was bound to TiO$_2$ as 3-TiO$_2$ for characterization of the covalently bound complex using attenuated total reflectance (ATR) FTIR spectroscopy.

The proposed structure 3-TiO$_2$ or 3-nano-ITO (Scheme 1) follows from the characterization data. Although ATR-FTIR spectroscopy has been previously used to study porphyrins on metal oxide surfaces, nano-ITO and 3-nano-ITO surfaces are unsuitable 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-visible spectroscopy could not be used for characterization of 3-TiO$_2$ or 3-nano-ITO (Figures S1 and S2). However, ATR-FTIR spectroscopy was available for 3-TiO$_2$ with a hydroxylated surface analogous to 3-nano-ITO. We found that the ATR-FTIR spectra of 3 and 3-TiO$_2$ (Figure 1) are very similar.

The silatrane cage ATR-FTIR bands of 3 at 1452 cm$^{-1}$ for $\delta$(CH$_2$) and 1170 cm$^{-1}$ for $\nu$(C–O) disappear upon formation of 3-TiO$_2$ by surface binding, as previously observed for other systems, including porphyrin-silatranes bound to metal oxide surfaces. The functional groups C–O (1689 cm$^{-1}$ stretch), N–H (1515 cm$^{-1}$ bend), C–C (pyridine alkoxide, 1590 cm$^{-1}$ stretch), C–H (alkoxide methyls, 2856, 2916, and 2960 cm$^{-1}$) and C–H (alkyl methyls, 2856 and 2960 cm$^{-1}$) bands were identified in the ATR-FTIR spectra of 3 and 3-TiO$_2$ and appear close to the theoretically determined values (within 25 cm$^{-1}$), thus supporting our assignments (Table S1). The complex seems to remain intact upon binding. In particular, the IR data suggest that the Cp$^\star$ ring remains bound to iridium upon surface binding and that the amide bond is still present. The IR assignments were identified by comparing ATR-FTIR spectra of 3 and 3-TiO$_2$ to Na[Cl$_2$Ir(2-(2-pyridyl)-2-propanolate)]$_2$, Cp$^\star$Ir(2-(2-pyridyl)-2-propanolate)Cl, 7 (Scheme S1), 7-TiO$_2$, p-tolyl silatrane, and p-tolyl-silatrane-TiO$_2$ (Figures S13–S19).

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

The DFT-IR spectrum of 3-TiO$_2$ 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 [101] surfaces of TiO$_2$, anatase. The model includes 6 TiO$_2$ units capped with hydroxides to ensure realistic modeling consistent with neutral pH conditions. The calculated ATR-FTIR spectrum of 3-TiO$_2$ shows good agreement with experimental bands in the 1000–1800 cm$^{-1}$ region, suggesting that the monomeric catalysts are not significantly interacting with each other. Deviations in the 2800–3100 cm$^{-1}$ region suggest some level of inhomogeneity not captured by a single configuration (Figures S11 and S12).

The electrochemical analysis of the 3-nano-ITO system in aqueous 0.1 M KNO$_3$ at pH 5.8 shows a redox couple at 0.9 V vs NHE (Figure 3a) assigned to the Ir(III/IV) couple. A similar couple is seen for 2 and 2-nano-ITO. The CV of 3 in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile shows an Ir(III/IV) redox couple at 0.93 V vs NHE and what may be an Ir(IV/V) redox couple at 1.35 V vs NHE (Figure 3b). Figure 3b shows a CV of 3-nano-ITO with a catalytic wave, suggesting that water-oxidation catalysis is occurring when higher potentials are reached. When the scan rates of the 3-nano-ITO were varied, a linear dependence of current versus scan rate was found, indicative of a surface-bound species (Figure S21).

Spectroelectrochemical experiments of 3-nano-ITO were also performed at 0, 1.35, and 1.55 V vs NHE.
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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) O₂ 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) O₂ 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 O₂ produced experimentally does not increase past 4.2 h. Theoretical O₂ evolution is also shown and was calculated based on the amount of charge passed during the electrolysis (dashed lines).

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

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

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

Heterogenized 3-nano-ITO was also studied electrochemically for water-oxidation catalysis. An O₂ assay was carried out using a Clark electrode. Data for 3-nano-ITO were collected under electrochemical conditions by first collecting a baseline 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 10 min period with no applied bias (Figure 4a). Oxygen was produced immediately when 1.35 V was applied, and Faradaic yields averaged 92% over the time frame studied (Figure 4a). The 3-nano-ITO catalyst has a 462 mV overpotential at pH 5.8, which is defined by the minimum applied potential required to measure O₂. An average turnover frequency of 0.035 ± 0.015 s⁻¹ for 3-nano-ITO was observed. A nano-ITO blank electrode did not evolve O₂ under the same conditions, suggesting that the O₂ produced in Figure 4a is from the iridium catalyst 3 (Figure S26). Additionally, nitrate has been suggested to participate in water-oxidation catalytic mechanisms when present in the chemical oxidant, cerium ammonium nitrate. To make sure that the catalyst could function without nitrate, 3-nano-ITO was also tested for electrochemically driven WO catalysis in sodium triflate, which was found to produce O₂ upon electrolysis (Figures S27 and S28).
frequencies of the Cp* methyl groups at 2856 and 2960 cm$^{-1}$, suggesting the oxidation of the Cp* ring and a shift in the N–H and C=C stretching frequencies due to a change in the iridium coordination sphere (Figure 5). We now represent 3′-TiO$_2$ as the structurally modified surface complex upon Cp* oxidation; however, the exact structure remains unknown. After 20 hours of electrolysis, only the alkyl C–H stretching bands assigned to the pyridine alkoxide ligand and the C=O stretch remain, so Cp* is likely removed at this point (Figure S19).

To understand how the Cp* loss affects catalysis, a long-term electrolysis was carried out on 3-nano-ITO with O$_2$ evolution measured as before (Figure 4b). After 4.2 h of electrolysis, the catalytic activity reached a maximum after 304 turnovers. Interestingly, the Faradaic yield is 82% up to 1.4 h but slowly decreases to 44% at 4.2 h. A chronoamperogram obtained during the electrolysis initially shows a stable current and then a rise in current after 1.4 h (Figure 6). Based on the ATR-FTIR process and thus may contribute to some of the nonproductive oxidation events. To probe this possibility, electrodes containing tolylsilatrane bound to nano-ITO, which should only show oxidation of triethanolamine, were prepared, and CV measurements were performed (Figure S24). Indeed, one irreversible oxidation event is observed for the first CV of the tolylsilatrane-nano-ITO electrodes, suggesting that oxidation of triethanolamine is possible. Upon running a second CV trace, the original signal disappears, which is indicative that the oxidation event is complete. Additionally, nano-ITO electrodes that have been sensitized with pure triethanolamine also follow the same CV trends as the tolylsilatrane-nano-ITO electrodes (Figure S25). Finally, formation of H$_2$O$_2$ is another possible oxidation event that could contribute to the lower Faradaic yields.

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

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