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Electrochemical Water Oxidation with Carbon-Grafted Iridium Complexes

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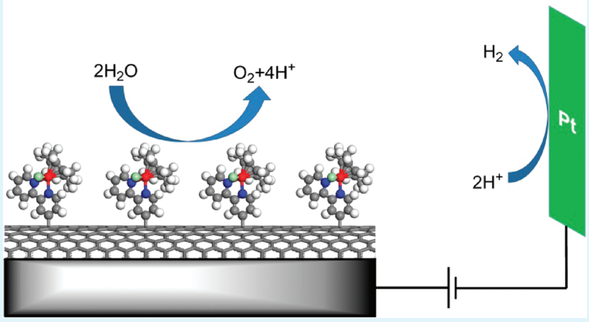
Supporting Information

ABSTRACT: Hydrogen production from water splitting provides a potential solution to storing harvested solar energy in chemical fuels, but this process requires active and robust catalysts that can oxidize water to provide a source of electrons for proton reduction. Here we report the direct, covalent grafting of molecular Ir complexes onto carbon electrodes, with up to a monolayer coverage. Carbon-grafted Ir complexes electrochemically oxidize water with a turnover frequency of up to 3.3 s^{-1} and a turnover number of 644 during the first hour. Electrochemical water oxidation with grafted catalysts gave enhanced rates and stability compared to chemically driven water oxidation with the corresponding molecular catalysts. This strategy provides a way to systematically evaluate catalysts under tunable conditions, potentially providing new insights into electrochemical water oxidation processes and water oxidation catalyst design.



KEYWORDS: *water oxidation, electrocatalysis, diazonium grafting, carbon electrode, water splitting*

Large-scale production of clean energy from renewable sources is needed to meet the growing global energy demand.[1] Among all the renewable energy sources, sunlight provides the most attractive long-term solution because of its vast abundance with an estimated solar radiation of 120 000 terawatts on the earth's surface. However, the diurnal and diffuse nature of local solar radiation makes it imperative to develop cost-effective storage of harvested solar energy. A potential solution is to store solar energy in reactive chemical bonds in the form of chemical fuels such as hydrogen or hydrocarbons.[2]

With the input of solar energy, hydrogen or hydrocarbons can be produced by water splitting or by CO_2 reduction with water, respectively. In both processes, catalytic water oxidation constitutes a key half reaction. The complex process of removing four electrons and four protons from two water molecules with concomitant formation of an O−O bond in this half reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) has made catalytic water oxidation a major challenge for several decades.[3−5] A large number of homogeneous water oxidation catalysts (WOCs) have been developed based on Ru complexes,[4,6−8] Ir complexes,[9−11] Fe complexes,[12,13] and polyoxometalates.[14−16] Several heterogeneous WOCs such as cobalt oxide[17−19] and iridium oxide nanoparticles[20,21] have been integrated into electrochemical or photoelectrochemical cells.[22−24] Ir complexes have also been doped into metal−organic frameworks to serve as heterogeneous WOCs.[25] All of these known WOCs, however, present many practical problems; molecular catalysts are prone to decomposition, whereas inorganic catalysts lack tunability. The progress on water oxidation catalysis, in fact, significantly lags behind the development of catalysts for the proton reduction half reaction ($2H^+ + 2e^- \rightarrow H_2$) of water splitting.[22,26−28]

The efficacy of a homogeneous water oxidation catalyst is typically evaluated by carrying out water oxidation with an external oxidant (such as Ce^{4+}, $E° = 1.72$ V) under strongly acidic conditions (e.g., pH <1). Some of these oxidants possess excessive oxidation power compared to the thermodynamic potential of 1.17 V at pH 1 for water oxidation, and can lead to the decomposition of otherwise stable catalysts. In solution, it can be difficult to determine if the initial complex is responsible for all catalytic activity or if it is a precursor to other catalytic species formed in situ. Alternative strategies are needed to assess the WOC potential of molecular complexes, particularly those based on earth-abundant first-row transition metals which tend to be more susceptible to decomposition. To this end, molecular Ir complexes were grafted onto carbon electrodes via covalent attachment and evaluated for electrochemical water oxidation.

Immobilization of molecular catalysts on electroactive surfaces is a key consideration in constructing solar water splitting devices. Placing the catalyst at an interface reduces the amount of catalyst needed and may enhance rates. Grafting WOCs onto electrodes can also potentially stabilize active

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intermediates and limit the extent of oxidative degradation. When grafted, molecules are spatially separated and will not deactivate via intermolecular pathways. Several homogeneous and heterogeneous WOCs have been immobilized onto electrodes for electrochemical water oxidation, either by anchoring molecular WOCs to oxide electrodes through phosphonate groups[29] or by deposition of nanoparticle or polyoxometalate WOCs onto electrodes.[17,30] We hypothesized that direct, covalent bonding of WOCs to the electrodes would allow enhanced catalytic rates and robust attachment, compared to existing immobilization strategies. Carbon electrodes are inexpensive and can be easily modified by chemical means.[31] Diazonium grafting is a well-established technique for covalent attachment of functional molecules to carbon electrodes.[32,33] Diazonium salts with suitable substituent groups are typically employed and can be used for anchoring other molecules via standard amide or other coupling chemistry. A molecular proton reduction catalyst has been, for example, anchored to carbon electrodes by this two-step grafting method through the formation of amide linkages.[27] We attached molecular WOCs to carbon electrodes in a single step using diazonium-functionalized derivatives of Ir complexes; analogous complexes are known to be active for chemically driven homogeneous water oxidation.[10]

This grafting strategy may allow for systematic evaluation of different molecular WOCs under tunable conditions that are more relevant to those found in a functional water splitting device, as opposed to evaluation in solution with a chemical oxidant with a fixed redox potential. The catalytic activities can be accurately determined as the amount of grafted catalyst can be quantified, even when redox peaks are not present, which is often the case. Grafting also allows the electrochemical response of WOCs to be studied without complications encountered in solution electrochemistry related to WOC adsorption, film formation, or insolubility. The grafting strategy also allows the measurement of WOC activities at various pH values which is not possible for Ce^{4+} and other inorganic oxidant driven water oxidation reactions.

Three new pentamethylcyclopentadienyl (Cp*)-Ir WOCs with amine pendant groups were synthesized. The complexes $[Cp^*IrCl(4\text{-}NH_2\text{-bpy})]Cl$ (bpy = 2,2′-bipyridine) (**A**) and $[Cp^*IrCl(5\text{-}NH_2\text{-bpy})]Cl$ (**B**), a pair of isomers, were synthesized by allowing one-half equivalent of $[IrCp^*Cl_2]_2$ to react with 4-NH_2-bpy or 5-NH_2-bpy. The complex $[Cp^*IrCl(p\text{-}NH_2\text{-ppy})]$ (ppy=2-phenylpyridine) (**C**) was synthesized similarly, but with *p*-NH_2-ppy instead of bpy to result in a neutral complex. These new complexes were characterized by NMR spectroscopy, mass spectrometry, and cyclic voltammetry (CV). **A**−**C** all show catalytic currents by CV in aqueous solutions (pH 5), consistent with electrochemically driven water oxidation (see Figure S1 in the Supporting Information). They were also shown to be active catalysts for water oxidation when driven chemically in aqueous solution (pH 1) with Ce^{4+} as the oxidant, by detecting O_2 in the headspace above the solution (see Figure S2 in the Supporting Information).

Each of the complexes was grafted onto glassy carbon electrodes by a direct, diazonium grafting method to lead to samples **1**−**3** (Figure 1). Prior to grafting, the electrode was polished and oxidized by applying a potential of 1.6 V vs the normal hydrogen electrode (NHE) for 2 min to obtain a reproducible background current, which is due to a combination of water oxidation and carbon oxidation.[34] The amino group of each complex was converted into a diazonium group in situ by addition of HCl and $NaNO_2$ to an aqueous solution of the complex, and $NaBF_4$ was added to stabilize the diazonium salt. The resulting solution was degassed and used for electroreduction of the diazonium salt by applying a potential of −0.4 V vs NHE for 4 min. Grafting was done on a 1.13 cm^2 area of the planar electrode. The grafted electrode was rinsed with water and methanol. Three samples were made identically for each catalyst in order to obtain averaged CV and catalyst loading data for determination of turnover frequencies (TOFs). The orientation of a complex relative to the surface is shown for **1** in Figure 1, which is modeled based on a published crystal structure for $[Cp^*IrCl(ppy)]$.[35]

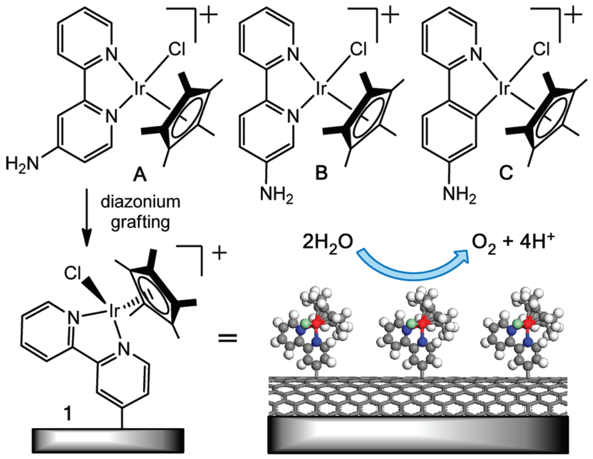

Figure 1. Molecular iridium WOCs have been covalently attached to carbon electrodes for efficient electrochemical water oxidation. Amino-functionalized derivatives (**A**−**C**) of WOCs were converted into diazonium salts, which were then grafted by electroreduction to result in functionalized glassy carbon electrodes **1**−**3**, respectively (only **1** is shown).

We first examined the electrocatalytic water oxidation activity of **1**-**3** by CV. The CV scans were carried out in the 0.2−1.6 V range vs NHE with a scan rate of 100 mV/s in an acetic acid/sodium acetate buffer at pH 5. A platinum counter electrode and Ag/AgCl reference electrode were used for all electrochemical experiments. Catalytic currents from water oxidation at 1.6 V are 226 ± 13, 16 ± 5, and 55 ± 9 $\mu A/cm^2$ over the background for **1**, **2**, and **3** respectively (Figure 2a). Compounds **A**−**C** thus retain their electrocatalytic activity toward water oxidation after being grafted on carbon electrodes. The background current was determined to be 93 ± 6 $\mu A/cm^2$ using an electrode that underwent electroreduction with a blank solution that was otherwise identical to a catalyst solution, and was subtracted from the currents of samples **1**−**3** (see the Supporting Information). The effects on current due to the electroreduction process and physisorbed catalysts have been eliminated, so that the reported currents represent only catalytic current from grafted molecules.

The Ir(III) complexes must reach a higher oxidation state before they are able to drive water oxidation. As with **A**-**C**, **1**−**3** do not show any clear redox couple in buffer. The lack of peaks is likely due to the slow proton migration rate of proton coupled electron transfer steps.[36] The redox events that occur at the onset of water oxidation may also be obscured by the catalytic wave.[9] Figure 2b shows CVs of **1** at different scan rates ranging from 20 to 400 mV, with the current normalized by dividing by the square root of the scan rate. The normalized catalytic current increases as scan rate decreases, indicating a

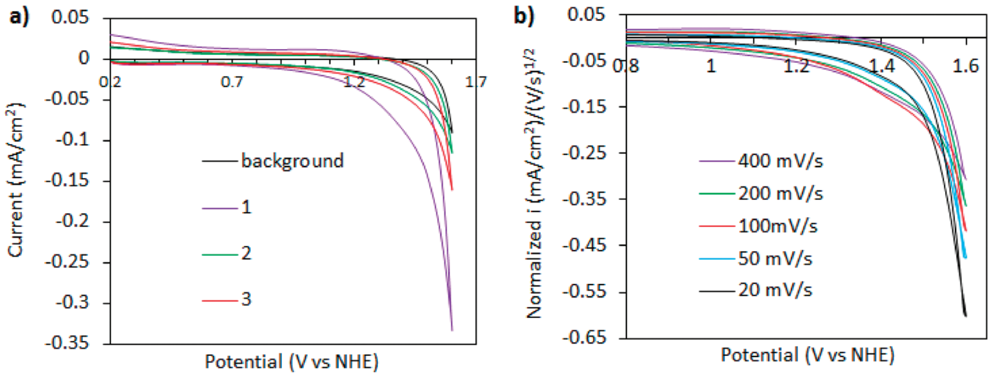

Figure 2. (a) Stabilized CVs for **1** (purple), **2** (green), and **3** (red) compared to background (black), at 100 mV/s in acetate buffer (pH 5). (b) Scan rate normalized CVs of **1** at 20, 50, 100, 200, and 400 mV/s, with background subtracted. Normalized *i* is the current in mA/cm^2 divided by the scan rate in V/s.

catalytic process with a rate-limiting chemical step before quick electron transfer.[36,37]

Catalyst loadings in samples **1**−**3** were determined by inductively coupled plasma mass spectrometry (ICP-MS). The grafted complex was removed from the electrode using a piranha solution, and the amount of Ir was measured by ICP-MS. Catalyst loadings were quite different among **A**−**C**, with average loadings of 0.36, 0.091, and 0.043 nanomol/cm^2, corresponding to surface coverages of **A**−**C** at 2.18, 0.55, and 0.26 molecules/nm^2 for **1**−**3**, respectively. The coverage on **1** is estimated to be about a monolayer. The loading efficiency may be related to the solubility of the complex in the solution used for grafting, as charged complexes **A** and **B** were completely soluble while neutral complex **C** was only slightly soluble and resulted in lower loading. The loading efficiency is also likely dependent on the reduction potential needed to initiate the grafting reaction in each case. The reduction potential at which grafting occurs is not clear due to the overwhelming background reduction current at 0.2 to −0.4 V.

The TOF for each catalyst was calculated based on the current at 1.6 V and the catalyst loading as measured by ICP-MS. The TOF is the molecules of O_2 produced per molecule of catalyst per unit time, assuming 100% Faradaic efficiency (which is justified below). The ability to measure the amount of catalyst on the grafted electrodes provides an advantage over studying these WOCs electrochemically in solution. The solution CVs lack observable redox peaks (for reasons explained above), so TOFs cannot be calculated and compared among various catalysts. The potential of 1.6 V corresponds to an overpotential of 0.66 V, as the thermodynamic potential for water oxidation at pH 5 is 0.94 V vs NHE. The TOFs were 1.67 ± 0.25, 0.59 ± 0.34, and 3.31 ± 0.27 s^{-1} for **1**−**3**, respectively. The Cp*Ir complex with the more electron-donating ppy ligand, **3**, is a more active WOC electrochemically than either of the WOCs with a bpy ligand, as is also observed in chemically driven catalysis with Ce^{4+} as the sacrificial oxidant (see Figure S2 in the Supporting Information). It is apparent from the difference in TOF between **1** and **2** that the position of attachment on the pyridine ring affects the rate of water oxidation. Catalysis is significantly hindered when ppy is attached to GC at the 5 position, compared to the 4 position, presumably due to electronic effects or unfavorable interaction with the GC surface. Although unlikely, we cannot rule out the possibility that the carbon surface could mediate the catalytic reaction to cause different activity dependent on catalyst orientation. The overpotential used in Ce^{4+}-driven water oxidation is 0.55 V, since the thermodynamic potentials for Ce^{4+} reduction and H_2O oxidation at pH 1 are 1.72 and 1.17, respectively. The TOF for **A** in Ce^{4+} solution was only 0.0167 s^{-1} for the first hour, after which TOF decreased rapidly. At pH 5, a potential of 1.49 V would correspond to a 0.55 V overpotential, at which the TOF for **1** is 0.51 s^{-1}. This comparison demonstrates that faster catalytic rates can be achieved by evaluating molecular catalysts electrochemically rather than by using a chemical oxidant.

Table 1. Catalyst Current, Loading, and TOF[a]

sample	current[b] (μA/cm^2)	loading (molecules/nm^2)	TOF (s^{-1})
1	226 ± 13	2.18 ± 0.44	1.67 ± 0.25
2	16 ± 5	0.55 ± 0.16	0.59 ± 0.34
3	55 ± 9	0.26 ± 0.03	3.31 ± 0.27

[a] Averaged over three replicates. Error is standard deviation. [b] At 1.6 V, with background subtracted.

We further examined the stability of the carbon-grafted WOCs during electrochemical water oxidation reactions. A stability test was carried out on **1** over three hours (Figure 3a). Five functionalized electrodes were prepared identically, and controlled potential electrolysis was done at 1.6 V with three of them for 1, 2, or 3 h. The remaining two electrodes did not undergo electrolysis; one was only rinsed, and the other underwent ten CV scans. The sample that was only rinsed contained 4.83 molecules/nm^2. Much of this was lost during the 10 CV scans that resulted in a stable response, to leave 1.97 molecules/nm^2. The catalyst lost during the scans was likely not covalently bound. Most of the remaining bound catalyst is then lost more slowly over three hours of electrolysis, leaving 0.10 molecules/nm^2. The loss of catalyst is likely due to loss of carbon from the surface of the electrode, rather than catalyst decomposition, as carbon is oxidized at the potential used. It is not possible to determine TOF from the CV for catalyst remaining after electrolysis, because the background current increases a great deal during electrolysis. This increase is probably due to an increase in surface hydrophilicity and surface roughening, as observed by scanning electron microscopy (SEM), resulting in increased surface area (Figure 3b, c). The electrode surface still appears smooth after 40 min, when most of the grafted catalyst remains on the electrode. The roughening of the surface becomes apparent after 10 days of electrolysis, when no catalyst remains on the surface.

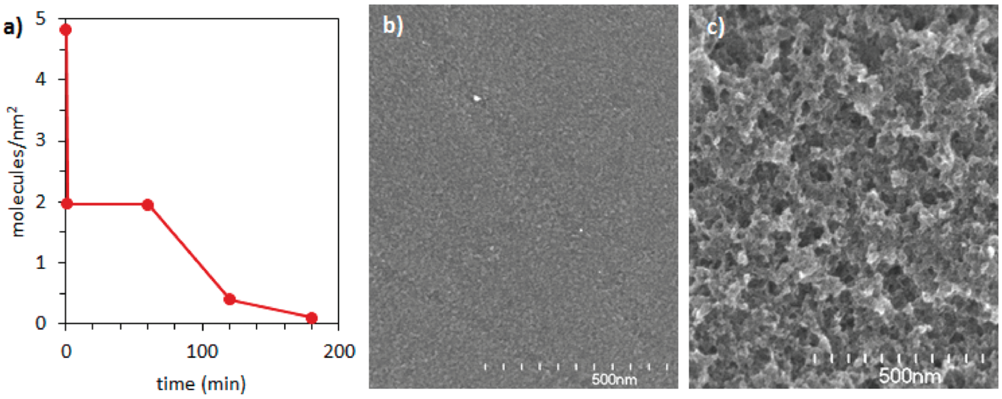

Figure 3. (a) Catalyst loading for **1** during controlled potential electrolysis in acetate buffer (pH 5) at 1.6 V. (b, c) SEM images of glassy carbon electrode **1** after (b) 40 min of electrolysis and (c) 10 days of electrolysis.

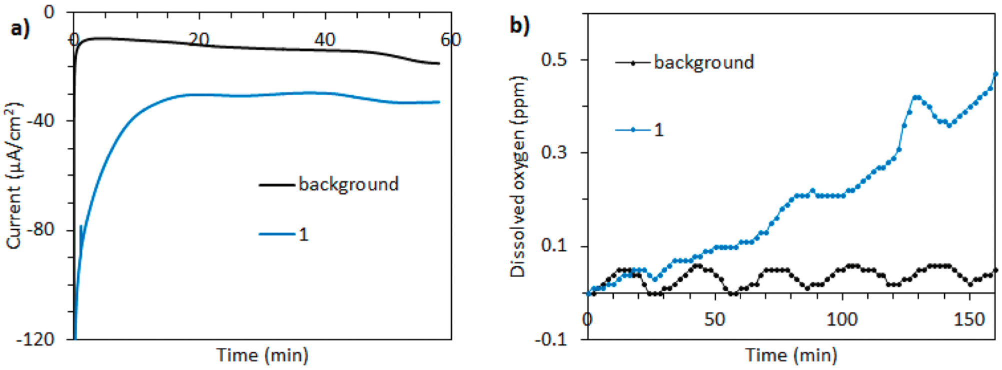

Figure 4. (a) Current during 1 h of electrolysis in acetate buffer (pH 5) at 1.6 V for **1** (blue) and a bare electrode (black). (b) In each case, oxygen was detected in solution during 60 min of electrolysis, and for 100 min afterward.

The current from **1** during 1 h of electrolysis can be compared to the current from a bare electrode to determine sustained TOF during electrolysis as well as TON after 1 h (Figure 4a). This type of measurement is problematic with molecular WOCs in solution because of the deposition of films on the electrode that contain electroactive species different from the catalysts in the bulk solutions.[38] After subtracting the background, the current at 1 h is 14.2 μA/cm^2, resulting in a TOF of 0.113 s^{-1}. The total charge passed by the catalyst in 1 h corresponds to 238 nmol of O_2 and a TON of 644 in 1 h. TON could be limited by oxygen bubble formation on the electrode, which is observed during electrolysis. Bubbles would prevent diffusion of water to the surface-bound WOCs. Even considering this, the TON for **1** is much higher than the TON of ~150 obtained before the same catalyst is nearly deactivated after 7.5 h of Ce^{4+}-driven water oxidation. This comparison suggests that the surface grafting strategy might have significantly stabilized the WOC, presumably by shutting down the intermolecular decomposition pathways. The possibility of catalyzed oxidation of the carbon electrode by the Ir-complexes was a concern; however, the background current increases nearly the same amount during an hour of electrolysis with both **1** and a blank electrode (see Figure S7 in the Supporting Information). If the Ir complex were catalyzing carbon oxidation, a greater increase in background current would be expected for the grafted electrode. A rapid loss of the complex from the electrode would also be observed, as it is anchored by C−C bonds, but there is very little loss of catalyst during the first hour of electrolysis. The loss of the molecular WOCs from the carbon electrode due to carbon oxidation makes it difficult to determine TOF or TON beyond 1 h. The catalytic activity seen for **1** during electrolysis is similar to the activity that can be achieved by attaching phosphonate derivatives of WOCs to electrode surfaces as reported by Meyer et al.[29] A phosphonate derivative of WOC [Ru(Mebimpy)(bpy)(OH_2)]$^{2+}$ (Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine) produced a sustained current of 14.8 μA/cm^2 at a loading of 0.12 nmol/cm^2 when electrolysis was performed at 1.85 V, giving a TOF of 0.36 s^{-1}. The method described here allows for comparable catalytic activity, considering the potential used here is 0.25 V lower.

Oxygen was detected in solution during 1 h of electrolysis with **1** at 1.6 V using a luminescence-based sensor (Figure 4b). Because the amount of oxygen generated is quite small, the distribution of oxygen in the bubbles on the electrode surface, in the solution, and in the headspace makes it difficult to directly quantify the oxygen generation Faradaic efficiency. We resorted to an indirect determination by comparison with electrochemical water oxidation with IrO_2 nanoparticles, which are known to produce O_2 from H_2O with 100% Faradaic efficiency.[21] A similar amount of O_2 is detected in the headspace when a similar amount of charge is passed by IrO_2 nanoparticles over the same period of time (see Figure S8 in the Supporting Information). The Faradaic efficiency for **1** can be considered close to 100% by comparison with the oxygen detected during water oxidation with IrO_2 nanoparticles. The background current has been subtracted when considering the amount of charge contributing to oxygen production. While there is a significant amount of charge passed while performing electrolysis with a bare electrode, there is virtually no O_2

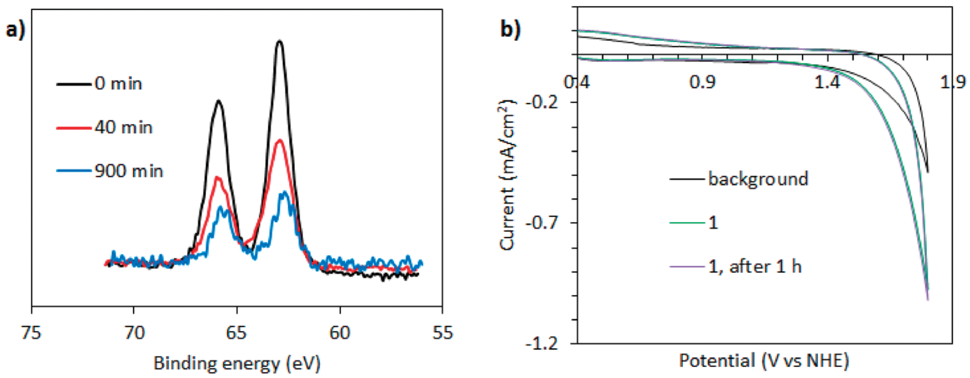

Figure 5. (a) XPS Ir 4f peaks from **1** after 0, 40, and 900 min of electrolysis at 1.6 V. b) CVs of **1** done in 0.1 M HNO_3 (pH 1) from 0.4 to 1.8 V with a scan rate of 100 mV/s.

detected. Most of this background current is likely due to oxidation of the carbon electrode, but the amounts of generated gases are too small to be detected by common methods like gas chromatography. The O_2 generation results confirm that the enhancement in current is not due to Ir-complex-catalyzed carbon oxidation. If much of the current from the grafted catalysts were coming from CO_2 generation, the amount of O_2 detected would be significantly lower than that detected during water oxidation with IrO_2. The same is true for CO_2 generation from oxidation of the organic ligands of the Ir complexes. In any case, only a small fraction of the current could be attributed to ligand oxidation due to the very small amount of catalyst used (~0.41 nmol). Oxidation of the acetate buffer is not a contributing factor under the conditions used, as CV scans on blank and grafted electrodes performed in 0.1 M KNO_3 (at pH 5) are similar to those performed in acetate buffer.

Grafting of molecular WOCs also allows for the identification of active catalytic species by surface spectroscopic measurements and other studies, which will help understanding of the electrochemical water oxidation reactions. For example, there is some concern that the formation of a metal oxide under the conditions used for water oxidation could be responsible for the catalytic activity of some molecular WOCs.[39,40] X-ray photoelectron spectroscopy (XPS) was carried out on **1** to rule out the formation of IrO_2 (Figure 5a). The Ir $4f_{7/2}$ peak was located at 62.9 eV for the Ir(III) complex on **1** after grafting, before any water oxidation was performed. The peak stays at the same binding energy after 40 min and even after 900 min of controlled potential electrolysis at 1.6 V. The Ir $4f_{7/2}$ peak for IrO_2 occurs at 61.6 ± 0.5 eV;[41] therefore, the XPS data indicate that the Ir complex does not turn into IrO_2 under the conditions used for water oxidation. The intensity of the Ir signal decreases over time because of loss of the complex from the surface, as discussed previously. Anchoring of the molecular WOCs also allows the water oxidation to be carried out at different pHs, providing further evidence against IrO_2 formation. IrO_2 is not stable at pH 1 and becomes inactive after ~30 min, as demonstrated by performing water oxidation with Ce^{4+} at pH 1. A sample of **1** was prepared and soaked in 0.1 M HNO_3 for 1 h, then 10 CVs were run from 0.2 to 1.8 V to stabilize the current (Figure 5b). The electrode was then soaked in 0.1 M HNO_3 for 1 more hour and 10 more scan cycles were performed before acquiring a second CV. Bare glassy carbon was treated in a similar manner as **1** for background comparison. A strong water oxidation wave is present for **1** and remains even after soaking at pH 1 for another hour. The retention of catalytic activity at pH 1 argues against the formation of IrO_2 as the active catalyst. Our results are in excellent agreement with a recent study by Crabtree, Brudvig, and co-workers using piezoelectric gravimetry to distinguish between homogeneous and heterogeneous catalytic water oxidation using molecular Ir complexes.[38]

Carbon oxidation, and thereby loss of grafted catalyst, is a potential problem when using glassy carbon at the oxidative potentials needed to drive water oxidation. However, this problem could be overcome by using a carbon electrode with a stable surface. Recently, a Ru-bis(terpyridine) complex was tethered to a conductive diamond electrode, and very little loss in electrochemical activity was observed after one million CV scans to 1.5 V vs NHE.[42] The issue of catalyst loss due to carbon oxidation as seen in the present study can be alleviated with the use of a conductive diamond electrode.

■ CONCLUSION

Grafting molecular Ir complexes directly and covalently to carbon electrodes demonstrates a new way to study molecular WOCs. As opposed to Ce^{4+}-driven water oxidation, electrochemical water oxidation using grafted WOCs can be carried out under tunable conditions, which is more relevant to identifying typically less stable molecular WOCs based on first-row transition metals. This method provides a more accurate way of assessing the true activity of a WOC without decomposition due to unnecessarily harsh conditions. Combining this new surface attachment strategy with newly developed molecular WOCs that are active and earth-abundant can lead to a potentially practical solution for storing solar energy in chemical fuels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures; synthesis and characterization of Ir complexes; solution CVs of **A**–**C**; additional CVs of **1**, bare glassy carbon, and grafting solutions; catalytic activity of **A**-**C** during Ce^{4+}-driven water oxidation; scan rate normalized currents; SEM images of electrodes; O_2 detection; XPS spectrum of **1**; water oxidation with IrO_2 nanoparticles. 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.

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