Noncovalent Immobilization of Electrocatalysts on Carbon Electrodes for Fuel Production

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S *Supporting Information*

ABSTRACT: We show that molecular catalysts for fuel-forming reactions can be immobilized on graphitic carbon electrode surfaces via noncovalent interactions. A pyrene-appended bipyridine ligand (**P**) serves as the linker between each complex and the surface. Immobilization of a rhodium proton-reduction catalyst, [Cp*Rh(**P**)Cl]Cl (**1**), and a rhenium CO_2-reduction catalyst, Re(**P**)-$(CO)_3$Cl (**2**), afford electrocatalytically active assemblies. X-ray photoelectron spectroscopy and electrochemistry confirm catalyst immobilization. Reduction of **1** in the presence of *p*-toluenesulfonic acid results in catalytic H_2 production, while reduction of **2** in the presence of CO_2 results in catalytic CO production.

Assembling systems for the conversion of solar photons into chemical fuels (i.e., artificial photosynthesis) requires the development of strategies for functionalization of electrode surfaces with catalysts.[1] One promising motif uses tandem semiconductors as light absorbers with catalysts mounted on surfaces to facilitate redox reactions.[2] Such reactions for solar fuel formation rely on catalytic processes for selectively reducing abundant feedstocks (e.g., water, carbon dioxide). Inorganic or organometallic complexes have attracted major attention as homogeneous catalysts; in principle, their mechanisms are molecular in nature, providing us the ability to control their specificity toward substrate. However, studying molecular reactivity on electrode surfaces[3] remains challenging, since immobilization methods are often not general; many methods are harsh and reduce the lifetimes of molecular catalysts.[4]

Our group has immobilized proteins[5,6] onto carbon electrodes by covalently attaching pyrene groups to polypeptide residues. Assembled cathodes are then competent for bioelectrocatalysis, without the use of redox mediators. In these proteins, electron transfer is facilitated by interactions between the pyrenyl groups and graphitic carbon surfaces. Similar approaches have been used to immobilize redox-active molecules on carbon electrodes, carbon nanotubes,[7] and even graphene sheets.[8] Here, we have appended pyrene groups to metal complexes as a general method for immobilizing molecular catalysts on electrode surfaces. Such a general method will be useful in evaluating molecular catalysts for applications in artificial photosynthesis.

Analogues of two previously reported catalysts were chosen as targets for immobilization: a rhodium proton-reduction

catalyst reported by Kölle and Grätzel[9] and the rhenium CO_2-reduction catalyst reported by Lehn and co-workers.[10] A modular route was designed wherein pyrenyl groups were first covalently attached to bipyridine by coupling 2,2′-bipyridyl-4,4′-carboxylic acid with 1-pyrenylmethylamine. The resulting ligand could then be metalated[11] to give complexes **1** and **2** (Figure 1; see Supporting Information (SI)).
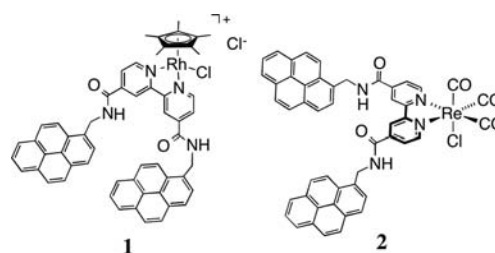

Figure 1. Pyrene-appended catalysts for immobilization.

A commercial high surface-area carbon black material (Ketjen black, AkzoNobel) was used as the substrate to afford conducting surfaces that support high electrocatalytic current densities with a high microscopic surface area.[12] Electrodes were prepared using a suspension of Ketjen black in *N*-methylpyrrolidone (containing a small amount of poly-(vinylidene fluoride) drop-cast onto the basal plane of highly oriented pyrolytic graphite (HOPG). After heating at 70 °C for 4 h, the electrodes were ready for catalyst immobilization (see SI). The electrodes were functionalized with a catalyst by soaking for 12 h in CH_2Cl_2 solutions containing **1** or **2** and then rinsed with clean, dry MeCN to remove loosely bound complexes.

The electrodes were interrogated by X-ray photoelectron (XP) spectroscopy. Before immobilization of our metal complexes, the surfaces showed only peaks for carbon (C 1s), nitrogen (N 1s), fluorine (F 1s), and a small contribution from oxygen (O 1s). Following preparation with **1**, new peaks appeared that are consistent with rhodium(III) (Rh 3d; Rh 3p; see Figure 2 and SI), chloride (Cl 2s; Cl 2p), and additional nitrogen (N 1s). XP spectra collected for electrodes soaked in solutions of an analogous complex not appended with pyrene ([Cp*Rh(phen)Cl]Cl; phen = 1,10-phenanthroline) did not show analogous peaks. Similarly, electrodes soaked in solutions containing **2** showed new XP peaks corresponding to
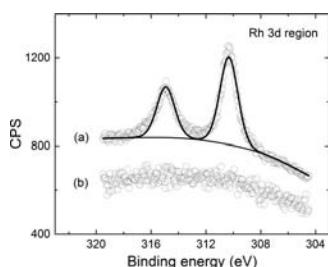
Figure 2. XP spectra in the Rh 3d region for (a) an electrode with immobilized **1** and (b) a clean electrode without immobilized catalyst. Data fit (black lines) shows Rh 3d peaks at 310.3 and 314.9 eV, consistent with rhodium(III) in **1**.

rhenium(I) (Re 4f, 4d), chloride (Cl 2s, 2p), and additional nitrogen (N 1s). Electrodes soaked in solutions of Re(bpy)-$(CO)_3Cl$ (**4**) (bpy = 2,2′-bipyridyl) showed no signal for rhenium or chloride (see SI for all spectra). We conclude that pyrene binding is responsible for the association between our complexes and the electrode surface.

Cyclic voltammograms of electrodes with immobilized **1** showed a feature centered at −0.8 V (all potentials are referenced versus $Cp_2Fe^{+/0}$, denoted $Fc^{+/0}$) (Figure 3).[13] The
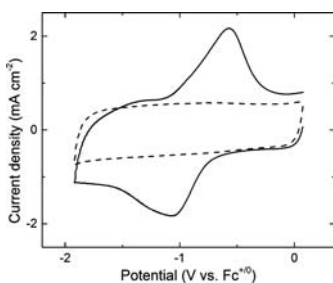

Figure 3. CV of **1** immobilized on a carbon black electrode (solid line) and a blank electrode background (dashed line). Conditions: scan rate, 150 mV/s; 0.1 M NBu_4PF_6 as supporting electrolyte in MeCN.

cathodic current peaked near −1.1 V and continued above background to near −2 V. The return anodic feature peaked near −0.56 V and was narrower than the cathodic feature. At 150 mV/s, the peak-to-peak separation (ΔE_p) was ~500 mV; scanning at lower scan rates gave smaller peak separation (see SI). The peak currents varied linearly with the scan rate of the voltammetry, consistent with a surface-immobilized redox species (see SI). The ratio of charge transferred upon reduction and reoxidation was also near unity (see SI).

[Cp*Rh(bpy)Cl]Cl (**3**) exhibited a reversible two-electron reduction near −1 V in MeCN.[9,14] For **1**, there was a similar reversible redox event at −1.1 V in CH_2Cl_2 (see SI). The $E_{1/2}$ of −0.8 V for immobilized **1** is consistent with these values, since the carboxamide substituents of **P** are electron-withdrawing. Reduction of **3** resulted in loss of the inner-sphere chloride ligand and formation of a five-coordinate Rh^I species. Similarly, the Cl^- signal was lost in XP spectra of electrodes after electrochemistry, while all other peaks remain unchanged. Since the redox process is coupled to the loss of chloride, the observed peak separation of greater than 60 mV was also expected.[15] Assigning this redox event as a two-electron process and using the total charge transferred gives a surface coverage of **1** of 26 nmol cm^{-2}, far higher than coverage expected for a planar electrode, attributable to the carbon black substrate used here.

Cyclic voltammetry of immobilized **2** gave a broad set of reductions with peaks at −1.34, −1.59, and −1.84 V (Figure 4).
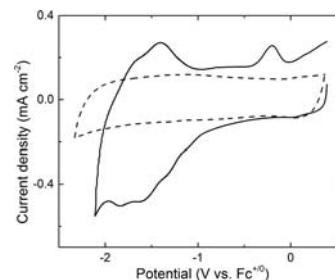

Figure 4. Electrochemistry of **2** immobilized on a carbon black electrode (solid line) and blank electrode (dashed line). Conditions: scan rate, 50 mV/s; 0.1 M NBu_4PF_6 as supporting electrolyte in MeCN.

These peaks compare well with redox events found for **2** in CH_2Cl_2 solution (see SI). A large return oxidation peak appeared at −1.4 V, with a shoulder at −1.7 V. An additional return peak was at −0.2 V; this peak appeared only with immobilized **2** upon cycling through the reductive events below −1 V. The ligand **P** (see SI) showed reductions at −1.21 ($bpy^{0/-}$) and −1.7 V with a return oxidation at −1.5 V.[16] For **2**, the first reduction at −1.34 V is assigned to dipyridyl-centered reduction, and the subsequent wave, to pyrene-centered reductions. The final redox wave at −1.84 V is assigned to a $Re^{+/0}$ couple. As in the case of **1**, the peak currents were linearly dependent on the scan rate, as expected for a surface-immobilized species (see SI).

Our assignments of the redox events for immobilized **2** agree with those of the solution analogue $Re(bpy)(CO)_3Cl$ (**4**): a bpy-centered reduction is followed by Re reduction that is coupled to loss of chloride.[17] XP spectra obtained after reductive cycling on electrodes with immobilized **2** show loss of Cl^- (see SI), consistent with the solution behavior. There are no major changes in the other XP peak positions following reductive cycling, although the peak intensities decrease, suggesting loss of material from the electrode during cycling.

In early work with electropolymerized films of the 4-methyl-4′-vinyl-2,2′-bipyridine analogue of **4**, an anodic wave near −0.2 V[18] was assigned to reoxidation of a Re−Re dimer. Thus, we propose that our redox event corresponds to reoxidation of $2[Re(P)(CO)_3]_2^{n+}$ formed on the surface upon reduction. Solution studies of **2** in dichloromethane showed a similar oxidation near −0.5 V (see SI). This finding suggests that there is conformational flexibility in our ligand architecture, which may be key since dimeric species have been shown to be likely intermediates in catalysis with **4**.[19]

We have found that surface-immobilized **1** is a catalyst for H^+ reduction. Loss of redox reversibility is observed upon H^+ addition to the electrolyte as p-toluenesulfonic acid (Figure 5)[20] and was apparent after the first addition of acid. Further additions resulted in higher catalytic currents and complete loss of reversibility in the redox event. In the absence of catalyst, only a minor increase in the observed cathodic current was observed (see SI). At an acid concentration of 14 mM, the catalytic current (minus background current) plateaued at a steady state current density slightly above 2 mA cm^{-2}. Using the surface loading data calculated above, this steady state current density corresponds to a turnover frequency of 0.95 s^{-1}.[15]

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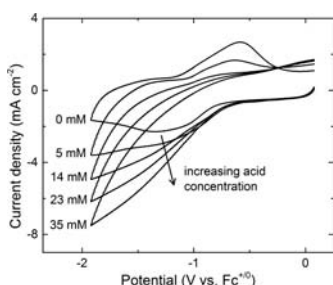
Figure 5. Changes in CV response of immobilized **1** in the presence of increasing concentrations of *p*-toluenesulfonic acid. Onset of catalytic response occurred near −0.75 V. Scan rate: 200 mV/s.

H_2 production was confirmed by gas chromatographic analysis of headspace gas in a closed two-compartment electrochemical cell during a controlled-potential electrolysis (CPE) of a 5 mM solution of *p*-toluenesulfonic acid. Over a 1.25 h period at −1.1 V, sufficient net charge was passed through the cell for production of 0.86 mL of gas. By GC, we found 0.90 mL of H_2, confirming essentially quantitative H^+ reduction (within ±10% error), and a turnover number (TON; mol of H_2 per mol of Rh on electrode) of 206. Notably, background current from the bare electrode produced a low faradaic yield (<20%) of detectable H_2 (<0.1 mL).

The CPE experiment reports on the stability of the attached catalyst. Over the course of the 1.25 h electrolysis, the catalytic current remained above background but steadily decreased at roughly 30% activity per hour, likely due to loss of catalyst from the electrode. XP spectra (see SI) showed decreased signals for Rh and N on the electrode surface following sustained CPE. Notably, XP spectra showed no indication of Rh metal or other reduced species following catalysis.

We have demonstrated that surface-immobilized **2** is a catalyst for the reduction of CO_2 to CO. A comparison of the cyclic voltammetry of an electrode with immobilized **2** under an atmosphere of argon (gray line) and carbon dioxide (black line) (Figure 6) showed that there is little change in the cyclic
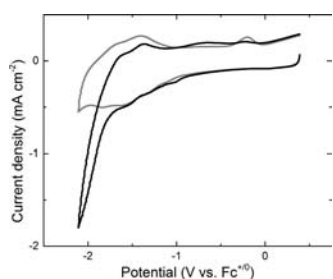

Figure 6. CV of immobilized **2** under Ar (gray line) and under CO_2 (black line). The scan rate was 50 mV/s.

voltammograms under CO_2 until the final reduction of **2** at ca. −1.8 V. The catalytic wave at this potential had a ratio of catalytic current to peak current (i_{cat}/i_p) of 3.6, similar to the enhancement observed for Re(bpy)(CO)$_3$Cl in solution, but lower than the 18.4 enhancement observed for a soluble di-*tert*-butyl-bipyridine analogue.[21] Notably, a clean electrode prepared without **2** showed negligible catalytic current under CO_2 (see SI).

GC analysis of headspace gas in a CO_2-purged cell following a 1.25-h electrolysis at −2.3 V confirmed the production of CO. Based on the net charge transferred, we predicted the

production of 0.39 mL of CO (assuming CO as the sole product).[22] By GC, we found 0.25 mL of CO, which corresponds to a faradaic yield of CO of 70% and a TON of 58. No H_2 was produced with immobilized **2**, but a small amount was found in control experiments without **2**.

We conclude that electrodes functionalized with **1** for H_2 production are more robust than those with **2** for CO_2 reduction. In the CPE of electrodes with **2**, the current reached background levels within the first hour of electrolysis (see SI). XP spectra of electrodes held at the deeply reducing potentials required for CO_2 reduction showed loss of Re from the surface on the time scale of these experiments (see SI). A possible explanation for this behavior could be reduction of the pyrenyl moieties at the very negative potentials required for operation of the catalyst; reduction of pyrene could result in electrostatic repulsion with the surface, or loss of planarity and binding.

In summary, we have shown that immobilization of molecular catalysts via pyrene groups is a promising general method for the construction of a cathode for the production of solar fuel. To the best of our knowledge, this is the first report of noncovalent surface attachment of a molecular CO_2 reduction catalyst. Encouragingly, despite the extreme potentials required for CO_2 reduction, we found these electrodes to be sufficiently stable for future exploration. Such comparisons will help in the optimization of functional assemblies for solar-driven water-splitting devices.

■ ASSOCIATED CONTENT

⑤ Supporting Information
Materials and methods; additional XP and electrochemistry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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