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Photochemical Preparation of a Film-Based Catalyst with Spatial Control

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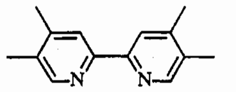
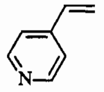
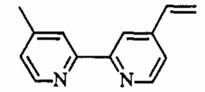
Polypyridyl-aqua complexes of ruthenium and osmium commonly exist in oxidation states higher than III as oxo complexes which are good oxidants and proven electrocatalysts for organic oxidations.[1-4] Recent work has shown that precursors to these complexes can be incorporated into polymeric films and that, to a degree, redox properties are maintained in the film environment.[5] In films there are interesting possibilities for using the oxo reactivity for sensors or electrocatalysis[6] and for creating multicomponent and spatially controlled microstructures.[7] We report here a novel approach to creating film-based electrocatalytic arrays based on the oxo chemistry with spatial control of the film pattern.



4,4',5,5'-tetramethyl-2,2'-bipyridine
(tmb)



4-vinylpyridine
(vpy)



4-vinyl-4'-methyl-2,2'-bipyridine
(vbpy)

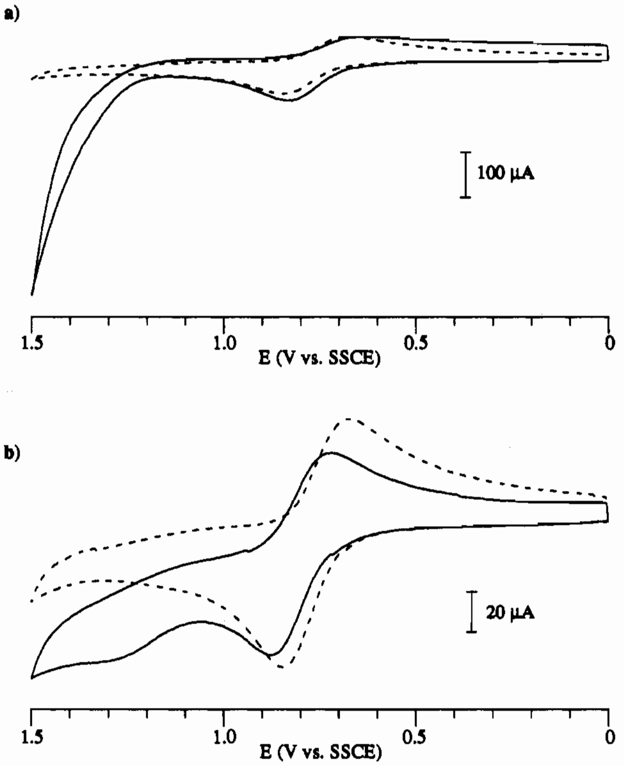


Figure 1. Cyclic voltammograms of poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$ coated glassy-carbon disk electrodes (3.0 mm diameter, $\Gamma = 1.2 \times 10^{-8}$ mol/cm^2) in (a) 0.1 M NaCl and 0.1 M CF_3CO_2H and (b) 0.1 M benzyl alcohol and 0.1 M CF_3CO_2H. Scans in the absence of added reductant (- - -) are also shown. Scan rate is 100 mV/s.

In previous work, films of poly-*cis*-$[Ru(tmb)_2(vpy)_2]^{2+}$ (tmb is 4,4',5,5'-tetramethyl-2,2'-bipyridine; vpy is 4-vinylpyridine) were prepared on Pt disk electrodes by reductive electropolymerization.[8] Polymerization occurs via a chain propagating, radical anion mechanism involving the vinyl-containing pyridyl ligands.[9] Because there are two vpy ligands per complex, the films are cross-linked by bonds between the vpy groups. Photolysis breaks the Ru–vpy bond removing the cross-link and provides a basis for photoetching with resolution below 10 µm.[7c] Here we exploit the photolability of pyridine but in films of poly-*cis*-$[Ru(vbpy)_2(py)_2]^{2+}$ (vbpy is 4-vinyl-4'-methyl-2,2'-bipyridine; py is pyridine) where the links of the polymeric network are photochemically stable.[7d] Photolysis in 0.1 M $HClO_4$ yields the bis(aqua)-substituted polymer, reaction 1. This is apparent by the

$$\text{poly-}cis\text{-}[Ru(vbpy)_2(py)_2]^{2+} + 2H_2O + 2H^+ \xrightarrow[(0.1\ M\ HClO_4)]{h\nu} \text{poly-}cis\text{-}[Ru(vbpy)_2(H_2O)_2]^{2+} + 2Hpy^+ \quad (1)$$

disappearance of the $Ru^{III/II}$ wave for poly-*cis*-$[Ru(vbpy)_2(py)_2]^{2+}$ at $E_{1/2} = 1.00$ V (vs. SSCE at pH 1.0 in 0.1 M $HClO_4$), and the appearance of a wave for poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$ at 0.71 V. No evidence of poly-*cis*-$Ru(vbpy)_2(py)H_2O)]^{2+}$ ($E_{1/2} \approx +0.90$ V)[10] was observed with photolysis times as short as 10 s. On an optically transparent, tin-doped indium oxide electrode, the low-energy MLCT absorption maximum for poly-*cis*-$[Ru(vbpy)_2(py)_2]^{2+}$ at 460 nm shifts to 486 nm upon formation of poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$ with 0.1 M $HClO_4$ in the external solution. In the pH range 1.5–4.4, a wave for the higher oxidation state $Ru^{VI/V}$ couple poly-*cis*-$[Ru^{VI}(vbpy)_2(O)_2]^{2+}$/poly-*cis*-$[Ru^{V}(vbpy)_2(O)_2]^+$ appears at 1.03 V.[1a] For the $Ru^{III/II}$ couple, $E_{1/2}$ decreases by ~60 mV/pH unit as is expected for the couple poly-*cis*-$[Ru^{III}(vbpy)_2(OH)(H_2O)]^{2+}$/poly-*cis*-$[Ru^{II}(vbpy)_2$-

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(8) Polymerizations were carried out in an inert atmosphere glovebox by using a standard three-electrode cell and acetonitrile soutions containing between 1.0 and 1.5 mM of the complex and 0.1 M $[N(n\text{-}C_4H_9)_4PF_6]$ (TBAH). The reference electrode was 0.01 M $AgNO_3$/Ag in 0.1 M TBAH/CH_3CN. The potentials cited are vs SSCE; the potential of the Ag^+/Ag couple vs. SSCE is –0.31 V.

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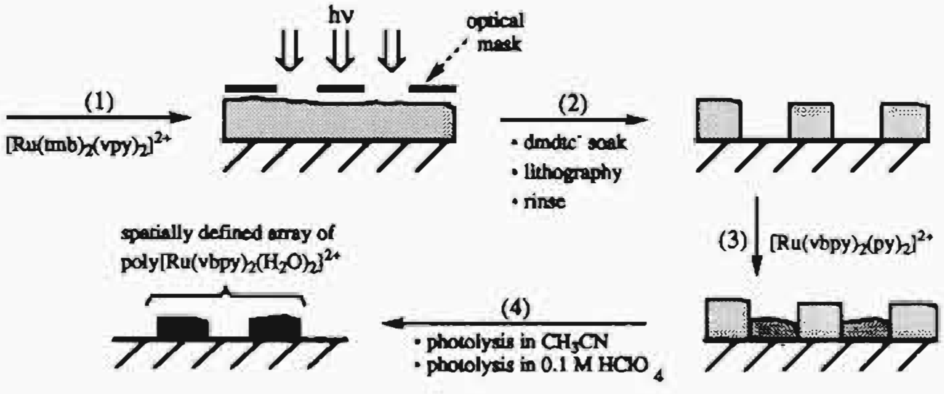
Scheme 1



$(H_2O)_2]^{2+}$. Well-defined waves for the intermediate $Ru^{IV/III}$ and $Ru^{V/IV}$ couples were not observed in the cyclic voltammograms.

Catalytic properties characteristic of the ruthenium oxo complexes in solution[1c,11] are retained in these films on glassy-carbon or reticulated-vitreous-carbon electrodes. Oxidative cyclic voltammetry at the $Ru^{VI/V}$ wave in the presence of added Cl^- or benzyl alcohol results in catalytic waves, $E_p = 1.34$ V (Cl^-) and $E_p = 1.30$ V (benzyl alcohol), Figure 1, whose peak currents increase with the concentration of reductant. The exclusive product of benzyl alcohol oxidation is benzaldehyde, as identified by GC/MS analysis of the solution following large scale electrolysis on reticulated vitreous carbon. The catalytic currents are not sustained. Electrolysis of a solution 0.1 M in CF_3CO_2H and 0.1 M in $C_6H_5CH_2OH$ at 1.35 V at a 0.071 cm^2 glassy-carbon electrode ($\Gamma = 1.2 \times 10^{-8}$ mol cm^{-2}) occurred with an initial current of 425 μA which fell to 11 μA in 5.5 h after 43.0 mC had passed.[12] The full catalytic activity of the film was restored by holding the electrode potential at 0.0 mV for 5 min in 0.1 M CF_3CO_2H and then cycling ten times between 0.0 and 1.5 V.

We have prepared spatially defined arrays of the electrocatalytic film by using the procedure depicted in Scheme 1. In the first step, poly-*cis*-$[Ru(tmb)_2(vpy)_2](PF_6)_2$ was formed on a 3.0-mm-diameter glassy-carbon disk electrode by repeatedly cycling to −1.9 V. The electrode was photolyzed by using contact lithography and an optical mask,[15] after incorporation of dimethyldithiocarbamate anion ($dmdtc^-$) by ion exchange to yield $[Ru(tmb)_2(dmdtc)]^+$ as the photoproduct.[7c] The photolyzed regions of the film were solubilized by rinses in acetonitrile and water. The second component was electropolymerized selectively in the exposed region by repeated cycles to −1.4 V (step 3).[7c] Subsequent photolysis in acetonitrile and then 0.1 M $HClO_4$ was used both to remove the remaining poly-*cis*-$[Ru(tmb)_2(vpy)_2]^{2+}$ and create a spatially defined array of poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$ as shown in reaction 1. In Figure 2 is shown a microscope photograph of a catalytic microstructure fabricated on a 3.0-mm-diameter glassy-carbon disk electrode. Spots of poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$ are visible, each having a diameter of 375 μm and a surface coverage of $\sim 6.2 \times 10^{-9}$ mol/cm^2.[13] The features on the electrode surface coincide well with the mask used to generate the pattern.[14]

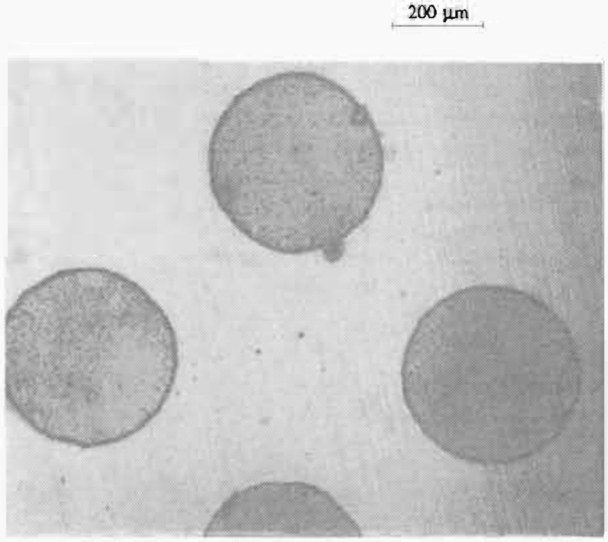


Figure 2. Optical microscope photograph of a 3.0-mm-diameter glassy-carbon disk electrode modified as shown in Scheme 1. The features on the electrode surface are 375-μm spots of poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$, which coincide well with the mask used to generate the pattern.

An important implication of these results is that a combined electrochemical–photochemical procedure is now available for preparing arrays of catalytic polypyridyl complexes on conducting substrates with spatial control. This may be important inelectrocatalysis where these complexes have been shown to act as film-based catalysts for reactions as diverse as the oxidation of water,[15] and reduction of CO_2.[16]

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(12) Electrolyses were carried out in three compartment cells with stirred 6-mL solutions. The potential was held at +1350 mV vs SSCE. GC/MS analysis was accomplished by extracting the electrolysis solution with dichloromethane, concentrating the organic layer, and injecting a 1-μL sample onto the GC. Retention times and mass spectra were compared to known samples of benzaldehyde and benzyl alcohol.

(13) Surface coverages were calculated from the integrated charge under the $Ru^{III/II}$ wave in cyclic voltammograms measured in fresh, electrolyte-containing acetonitrile solutions.

(14) The optical masks were prepared by using commercially available, high contrast, 35-mm slide film. The optical mask that was used was a 3 × 3 array of transparent circles, each 375 μm in diameter with a center to center separation of 600 μm.

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