

Sensitization of Nanocrystalline TiO₂ by Electropolymerized Thin Films

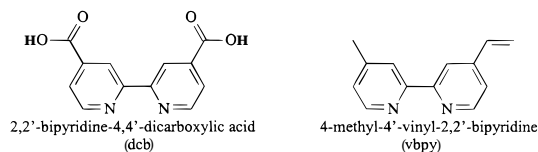
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Visible sensitization of nanocrystalline TiO₂ by adsorbed polypyridyl complexes of ruthenium has provided a basis for the development of a family of solution-based photovoltaic devices for energy transduction.^{1–8} We report here a novel approach to the preparation of thin-film structures on TiO₂ formed by reductive electropolymerization. The resulting structures open new possibilities for the fabrication of surface microstructures and stabilization of the dye–metal oxide interface.

The adsorption to acidic oxide surfaces of carboxylic acid-containing salts such as [Ru(dcb)₃](PF₆)₂ (dcb is 2,2'-bipyridine-4,4'-dicarboxylic acid)⁹ is well estab-



lished.^{1,3,5,6,10,11} Adsorption of the vbpy derivative [Ru(vbpy)₂(dcb)](PF₆)₂ (**1**; vbpy is 4-methyl-4'-vinyl-2,2'-bipyridine) from CH₃CN solution onto optically transparent, 8–12 μm thick films of nanocrystalline TiO₂ on In₂O₃:Sn (ITO) electrodes on glass¹² results in highly

absorbing films (TiO₂/Ru^{II}_{ad}) with OD ~ 1.2–1.8 at the metal-to-ligand charge transfer (MLCT) maximum at 467 nm.¹³

In cyclic voltammograms at 5 mV/s, oxidation of [Ru(vbpy)₂(dcb)](PF₆)₂ adsorbed by soaking the electrode in an acetonitrile solution 5 mM in complex is observed, with the Ru^{III/II} couple appearing at $E_{1/2} = +1.37$ V versus SSCE in CH₃CN 0.1 M in [(n-C₄H₉)₄N](PF₆) (TBAH) compared to +1.35 V in solution. Reductive scans from -0.4 V to -1.7 V at 100 mV/s in 0.1 M TBAH in CH₃CN with 0.05 mM [Ru(vbpy)₃](PF₆)₂ added exhibit a large, featureless reductive wave for TiO₂ with an onset at ~ -0.5 V. At these potentials, stable, thin films of poly[Ru(vbpy)₃](PF₆)₂ form on a variety of conducting substrates including Pt, glassy carbon, and ITO.^{14–18} On TiO₂ they result in copolymeric, overlayer thin films of poly[Ru(vbpy)₃](PF₆)₂ on [Ru(vbpy)₂(dcb)](PF₆)₂ (TiO₂/Ru^{II}_{ad}/poly-Ru^{II}). The mechanism of electropolymerization involves reduction at π*(vbpy) followed by radical polymerization.¹⁵ The TiO₂ electrodes deepen in color upon reduction, but this is reversed when the electrode is scanned oxidatively.

Evidence for electropolymerization is seen as an increase in absorption at 464 nm and in peak current for the Ru^{III/II} wave in cyclic voltammetry. The waves for the adsorbed and electropolymerized complexes overlap. The rate of electropolymerization is dependent on the amount of adsorbed complex,¹⁹ the number of reductive scans, and the concentration of [Ru(vbpy)₃](PF₆)₂ in the external solution. By absorbance monitoring at 464 nm, the amount of electropolymerized complex increases linearly with the number of reductive scans. For an electrode of initial surface coverage 1.2×10^{-7} mol cm⁻²,²⁰ a 2-fold increase in absorbance at 464 nm was observed after ~40 cycles with 0.1 M TBAH–CH₃CN 0.05 mM in [Ru(vbpy)₃](PF₆)₂ in the external solution. In previous work, it was shown that electropolymerization of [Zn(vbpy)₃](PF₆)₂ on ITO electrodes occurs at a rate comparable to that for [Ru(vbpy)₃](PF₆)₂.²¹ Ruthenium/zinc-modified TiO₂ surfaces (TiO₂/Ru^{II}_{ad}/poly-Zn^{II}) were prepared under the same conditions except with [Zn(vbpy)₃](PF₆)₂ in the external solution. The Zn^{II} complex is colorless and electrochemically inert to oxidation within the solvent limit.

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(19) The rate of polymer growth increases with surface coverage of adsorbed [Ru(vbpy)₂(dcb)](PF₆)₂. As the amount of adsorbed complex increases, the polymerization rate increases dramatically.

(20) Surface coverages (in mol cm⁻²) were determined from the absorbance at 464 nm, $A(464)$, by using the relationship, $A(464) = 1000\epsilon(464)\Gamma$ with $\epsilon(464) = 13\,000\text{ M}^{-1}\text{ cm}^{-1}$.

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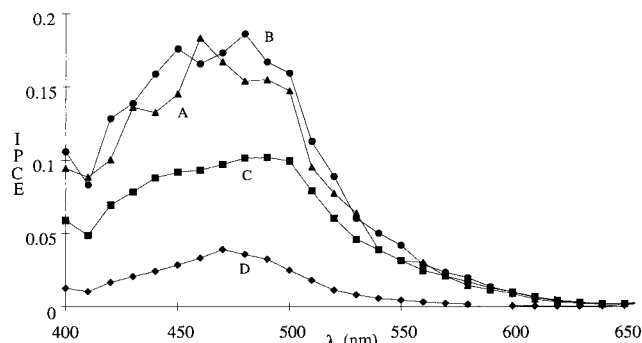


Figure 1. Plot of IPCE(λ) versus λ in propylene carbonate 0.5 M in NaI and 0.05 M in I_2 for colloidal TiO_2 thin film electrodes sensitized with (A) adsorbed $[Ru(vbpy)_2(dcb)]^{2+}$ (TiO_2/Ru^{II}_{ad}) (\blacktriangle), (B) adsorbed $[Ru(vbpy)_2(dcb)]^{2+}$ and electropolymerized $[Zn(vbpy)_3]^{2+}$ ($TiO_2/Ru^{II}_{ad}/poly-Zn^{II}$) (\bullet), (C) adsorbed $[Ru(vbpy)_2(dcb)]^{2+}$ and electropolymerized $[Ru(vbpy)_3]^{2+}$ ($TiO_2/Ru^{II}_{ad}/poly-Ru^{II}(\sim 1:1)$) (\blacksquare), and (D) electropolymerized $[Ru(vbpy)_3]^{2+}$ (\blacklozenge).

Tapping mode AFM measurements were conducted on a Nanoscope III from Digital Instruments, under ambient conditions with a resonance frequency of ~ 300 kHz by using silicon cantilevers on TiO_2 , TiO_2/Ru^{II}_{ad} , and $TiO_2/Ru^{II}_{ad}/poly-Ru^{II}$, the latter with a 1:1 ratio of $[Ru(vbpy)_2(dcb)](PF_6)_2$ to $poly[Ru(vbpy)_3](PF_6)_2$. These measurements, combined with optical microscopy, reveal that the surface coverage is uniform and homogeneous, at least to a resolution of ~ 500 nm.

Photoelectrochemical measurements were carried out in a thin-layer, two-electrode arrangement with propylene carbonate 0.5 M in NaI and 0.05 M in I_2 , as described previously.²² Results, reported as incident photon-to-current efficiency (IPCE), are illustrated for a series of derivatized electrodes in Figure 1. For TiO_2/Ru^{II}_{ad} , IPCE values as high as 20–25% were obtained with excitation at 464 nm compared to 35–40% for *cis*- $Ru(dcb)_2(NCS)_2$ ³ under the same conditions on identical electrodes. For $TiO_2/Ru^{II}_{ad}/poly-Zn^{II}$ with Zn^{II}/Ru^{II} ratios up to 2:1,²³ IPCE values were the same as for TiO_2/Ru^{II}_{ad} . For $TiO_2/Ru^{II}_{ad}/poly-Ru^{II}$, IPCE decreases with increasing polymer surface coverage with IPCE falling to 10–12% at a 1:1 $Ru^{II}_{ad}/poly-Ru^{II}$ ratio, reaching a limiting value of $\sim 3\%$ at ratios greater than 1:4 $Ru^{II}_{ad}/poly-Ru^{II}$.

One advantage to the electropolymerized, overlayer structures is enhanced stability, presumably caused by the formation of a cross-surface covalent bond network in the electropolymerization procedure. For example, for adsorbed $[Ru(vbpy)_2(dcb)](PF_6)_2$ in water, $>50\%$ loss of complex occurs with soaking at pH 2 for 30 min and 100% after 10 min at pH 14, as shown by absorbance monitoring. For 2:1 or larger $Ru^{II}_{ad}/poly-Ru^{II}$ ratios, stability at pH 1–14 was observed for a period of over 3 weeks. Because of the lability of Zn^{2+} in aqueous solution, $\sim 86\%$ of adsorbed $[Ru(vbpy)_2(dcb)](PF_6)_2$ on a $TiO_2/Ru^{II}_{ad}/poly-Zn^{II}$ surface is lost at pH 7 after 30 min. The remaining 14% was stable to desorption for over 3 weeks.

Under the same conditions as for $[Ru(vbpy)_2(dcb)](PF_6)_2$, $[Ru(vbpy)_3](PF_6)_2$ adsorbs to TiO_2 films but at $\sim 15\%$ of the loading level. Electropolymerization occurs

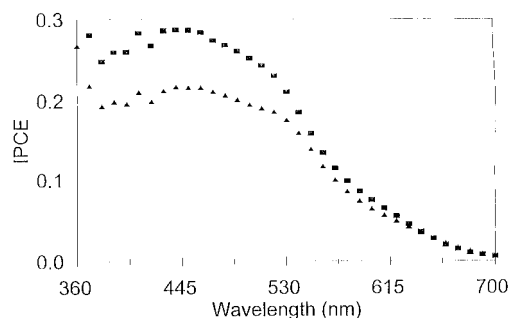


Figure 2. As in Figure 1, with adsorbed $[(bpy)_2(NC)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2]^{2+}$ (\blacksquare) and adsorbed $[(bpy)_2(NC)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2]^{2+}$ with electropolymerized $[(bpy)_2(NC)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2]^{2+}$ (\blacktriangle).

upon reduction of solutions containing this salt, but compared to films of $TiO_2/Ru^{II}_{ad}/poly-Ru^{II}$, the growth rate of the polymer is slower. At comparable total Ru loadings, as shown by absorption measurements, IPCE is lower by $\sim 75\%$ for the electropolymerized films.

The adsorbed assembly $[(bpy)_2(CN)Ru(CN)Ru(dcb)_2(NC)Ru(CN)(bpy)_2](PF_6)_2$ has been shown to have IPCE values in excess of 80% under the experimental conditions described here.^{1,7} The *vbpy* derivative $[(bpy)_2(CN)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2](PF_6)_2$ adsorbs on nanocrystalline TiO_2 films at a level $\sim 50\%$ that of $[Ru(vbpy)_2(dcb)](PF_6)_2$. Electropolymerization with $[(bpy)_2(CN)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2](PF_6)_2$ in the external solution²⁴ results in a total surface coverage ~ 2 times that of the adsorbed trimer. An IPCE of 29% with excitation at 440 nm was measured for the electropolymerized film compared to 22% for the adsorbed trimer (Figure 2). Correcting for the increased absorption in the electropolymerized film (from $A = 0.39$ to $A = 0.65$) by dividing IPCE by the light harvesting efficiency, $(LHE(\lambda) = 1 - 10^{-A(\lambda)})$ gives comparable, absorbed photon-to-current efficiencies $[APCE(\lambda) = IPCE(\lambda)/LHE(\lambda)]$ of $\sim 37\%$ for the electropolymerized and adsorbed trimer surfaces.

These results demonstrate that reductive electropolymerization can be used to prepare interfacial, polypyridylmetal complex structures on nanocrystalline TiO_2 films. This approach offers the advantage of creating highly stabilized surface structures but, for $TiO_2/Ru^{II}_{ad}/poly-Ru^{II}$, with significant loss of photocurrent efficiency. The origin of the decrease upon electropolymerization of an overlayer of $[Ru(vbpy)_3](PF_6)_2$ is currently under investigation. The results of a recent photophysical study on $poly[Ru(vbpy)_3](PF_6)_2$ have led to the suggestion that the electropolymerization procedure leads to the creation of trap sites which result in excited-state quenching.²¹ This can be avoided by use of nonchromophoric $[Zn(vbpy)_3](PF_6)_2$ as the cross-linking complex, but it decomposes in aqueous solution, leading to a loss of stability of the films. Films of $poly[(bpy)_2(CN)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2](PF_6)_2$ retain enhanced stability toward dye desorption while the conversion efficiency of the unpolymerized dye is main-

(23) The $Ru^{II}_{ad}/poly-Zn^{II}$ ratio was assumed to be the same as in films prepared under identical conditions with $[Ru(vbpy)_3](PF_6)_2$.²¹

(24) Electropolymerization was carried out on electrodes with adsorbed $[(bpy)_2(CN)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2](PF_6)_2$ under the same conditions as for $[Ru(vbpy)_2(dcb)](PF_6)_2$ with 0.1 M TBAH and 0.5 mM $[(bpy)_2(CN)Ru(CN)Ru(vbpy)_2(NC)Ru(CN)(bpy)_2](PF_6)_2$ in the external solution.

tained. Additional experiments are required to elucidate the photophysical mechanism of TiO₂ sensitization by electropolymerized films, but it seems clear that these systems provide a novel approach for the preparation and exploitation of stabilized assemblies on TiO₂ surfaces.

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