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Contribution from the Photoconversion Research Branch,
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Amelioration of the Photoresponse of PdPS Photoanodes by Ferrocyanide Electrolytes

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Crystals of the layered material n-PdPS were prepared. The photoresponse of these crystals was tested in a variety of redox electrolytes. Of the electrolytes tested, only ferrocyanide supported large photocurrents that were not associated with photocorrosion. The topographic photoresponse, studied by an in situ scanning laser technique, revealed that the highest quantum yields were associated with non van der Waals crystal surfaces. Mott–Schottky measurements in electrolytes with and without ferrocyanide suggest the adsorption of a negatively charged species. An interaction of the ferrocyanide with reactive edge sites of the PdPS crystal, resulting in a stable surface trap and interfacial charge mediator, is proposed.

Semiconductor electrodes have been used in a variety of energy conversion schemes;[2] however, studies concerning the influence of the surface structure, surface energetics and surface chemistry in the charge-transfer reactions at the electrode/electrolyte interface are not as common.[3-6] In this note we will show an example of an unusual chemical interaction with a ferrocyanide electrolyte resulting in enhancement of the photocurrent and photovoltage of a PdPS semiconductor photoanode. The interaction is deduced from the combination of photocurrent–voltage measurements, scanning laser photocurrent topography experiments and Mott–Schottky data.

PdPS as prepared by us is an n-type semiconductor with an indirect bandgap of 1.45 eV followed by a direct bandgap at 1.66 eV.[7] The synthesis and crystal growth of this material is described elsewhere.[7] The crystal structure of the material consists of a layer structure with two networks of square-planar palladium atoms making up a larger double layer.[8] Each palladium is coordinated to two S and two P atoms with a cis geometry between like atoms. The P and S atoms form $(S–P–P–S)^{4-}$ polyanions with the P–P units bridging intralayer palladium atoms (see Figure 1).

Initial photoelectrochemical studies revealed that among various redox electrolytes only ferrocyanate yielded high photocurrents not associated with photocorrosion. The photocurrents in a ferrocyanide electrolyte also had the remarkable quality of increasing rapidly with potential scanning under illumination in this redox electrolyte (Figure 2). Over time, the cell evolves from essentially no photoresponse to a light to electrical energy converting cell. The open-circuit voltage also increases from less than 100 mV to more than 350 mV during what we will henceforth call the amelioration process. In iodide solutions, for which the redox potential is close to that of ferrocyanide, only small photocurrents were observed. In iodide and bromide electrolytes photocorrosion was evident by the formation of pits and the disappearance of crystal planes associated with exposed edges. Presumably the photocorrosion is aided by the existence of stable soluble palladium halide complexes.

In situ laser scanning of the crystal surface[9] revealed that the photocurrents were higher in regions where microscopic examination revealed edge sites and steps. Figure 3 shows a laser scan of a PdPS crystal in a ferrocyanide solution and a drawing of the same crystal face showing the position of pyramidal steps and striations. Smooth cleavage surfaces showed little or no photocurrent even in ferrocyanide solutions. Maximum monochromatic (632.8 nm) quantum yields of up to 0.14 were measured by directing the laser beam on areas rich in edge sites. This behavior is opposite that of the group 6[21] transition-metal dichalcogenide semiconductors, which have severe surface recombination on non van der Waals faces.[10-12]

The Mott–Schottky behavior of a PdPS crystal was studied in a pH 8.8 phosphate buffer before and after the addition of ferrocyanide (Figure 4). Although the capacitance behavior is not ideal, the flatband potential shows a shift to more negative values (from −0.75 to −1.0 V vs. SCE) after amelioration by illumination in the ferrocyanide electrolyte as in Figure 2. The negative shift indicates that a negative charge is accumulated at the electrode surface. There is a slight change in the slope of the plot after amelioration, but a doping level of about 10^{17} cm^{-3} can be calculated from the average slope.

We would like to propose a model to explain the above results based on a specific interaction between the semiconductor surface and the ferrocyanide/ferricyanide species. We propose that the ferrocyanide binds to a vacant coordination site or sites at the edge of a layer of the PdPS crystal. The bridging cyanide provides a pathway for hole transfer to the iron center, which acts as an effective hole trap, which in turn mediates the hole transfer to the solution ferrocyanide. Increases in the hole-transfer rate have been shown to improve both the photocurrent and fill factor in photoelectrochemical devices.[13] This is due to a reduction of the recombination current, which competes directly with the interfacial charge-transfer reaction.

The layer structure of the material would most likely lead to anisotropy in the carrier mobility with a higher mobility along the layers. This anisotropy would tend to enhance hole trapping at the crystal edges exposed to the solution. Speculations about the band structure of PdPS suggest that a hole will not reside on the d levels of the metal atom because palladium(III)-like species are energetically unfavorable.[8] The top of the valence band, to which the holes will thermalize, has primarily phosphorus character,[8] and as a result, the initial step in photocorrosion is most likely the oxidation of the P–P or P–S bonds exposed at edges. In the process of photocorrosion vacant palladium coordination sites or reactive S or P radicals are exposed for bridging to a ferrocyanide species.

The resulting charge-transfer mediation between the bound ferricyanide and the solution ferrocyanide reduces photocorrosion. In one experiment we were unable to detect any change in the appearance of the surface of a thin (100–200 μm) crystal after passage of 100 C/cm^2 of photocharge. This charge would be sufficient to dissolve 40 μm of the crystal if the phosphorus and sulfur were oxidized completely to phosphate and sulfate.

The uniqueness of the ferrocyanide interaction is reinforced when $Ru(CN)_6^{4-}$ is substituted for the ferrocyanide in the redox electrolyte. No improvement of the small photocurrents was observed in this electrolyte. The redox potential of the ruthenium

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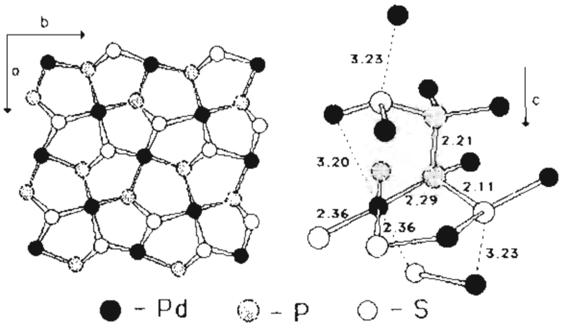

Figure 1. Top view of the net making up the cleavage planes of PdPS (left) and the local geometry and bond distances through a layer (right). The long (3.23 Å) distances are interlayer while the intralayer Pd–Pd distance is 3.20 Å.

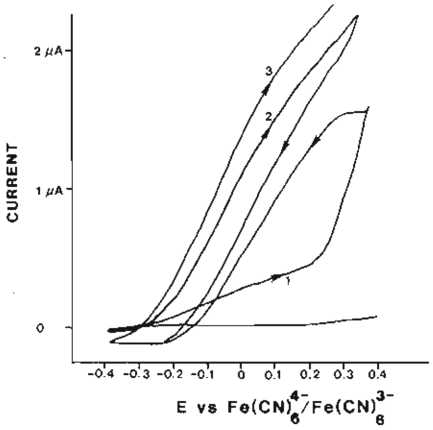

Figure 2. Two electrode current–voltage characteristics of a virgin PdPS electrode during potential scanning under illumination. The numbers designate the sequence of scanning in a solution of pH 8.8 phosphate buffer with 0.1 M $K_4Fe(CN)_6^{4-}$.

analogue is substantially more positive than that of the iron compound (0.74 V for $Ru(CN)_6^{4-}$ and 0.21 V for $Fe(CN)_6^{4-}$ vs. SCE), and as a result, holes in the valence band of PdPS (at a potential of about 0.45 V) are unable to oxidize the ruthenium complex and mediate charge transfer. In contrast, the ferrocyanide potential is ideally located just above the valence band potential.

The exact bonding configuration of the ferrocyanide species to the edge of the crystal is not known, but cyanide bridges between iron and palladium are known in inorganic complexes.[14] A macroscopic Prussian blue related phase, similar to those deposited on Pt and glassy-carbon electrodes[15,16] and observed to form on nickel[17] and cadmium sulfide[18] electrodes, is also a possibility. However no changes in the color or texture of the electrode surface could be observed even after extended illumination in ferrocyanide solutions. No prussian blue analogues of palladium have been reported in the literature[19] presumeably because its square-planar coordination geometry is incompatible with a Prussian blue type structure. Binding to a palladium through a S atom and formation of a thiocyanate bridge is another possibility that cannot be ruled out at this time.

The unique interaction between a solution redox couple and a group 8–10 transition-metal-containing semiconductor reemphasizes the importance of the surface chemistry of the semi-

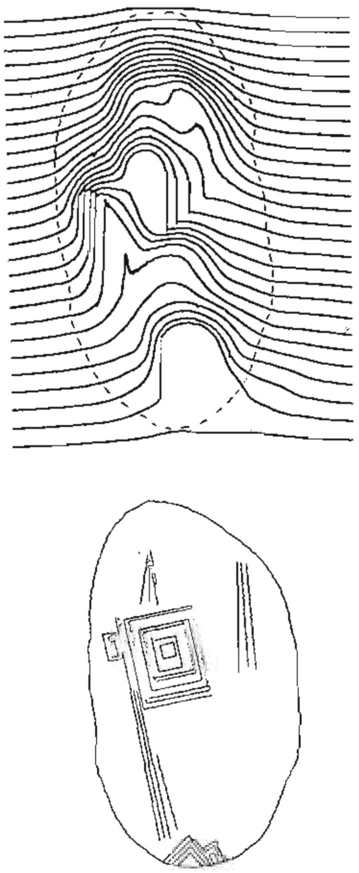

Figure 3. Top: laser scanning map of the topographic photoresponse of a PdPS crystal illuminated in the solution in Figure 2. Bottom: drawing showing the location of steps, dislocations, and striations on the PdPS crystal.

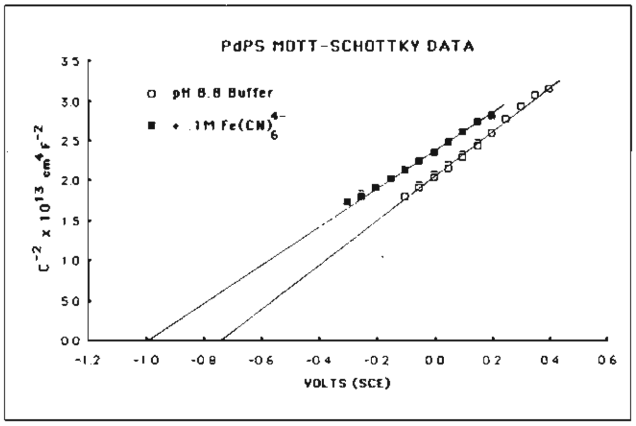

Figure 4. Mott–Schottky data for a PdPS crystal in pH 8.8 buffer (open squares) and after the addition of 0.1 M $K_4Fe(CN)_6^{4-}$ and amelioration of the crystal as described in the text (dark squares).

conductor electrode in the performance of a photoelectrochemical device. The systen also provides a model system for the study of the competition between charge transfer and recombination in quasi-two-dimensional semiconductor systems and perhaps will lead to more effective and stable methods to passivate recombination centers on other layered materials.[20] Indeed, specific

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(21) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

chemical interactions with a substrate will be the key to photoelectrocatalytic reactions of interest to solar energy conversion.

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Registry No. PdPS, 11083-63-9; $Fe(CN)_6^{4-}$, 13408-63-4; $Fe(CN)_6^{3-}$, 13408-62-3.

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^{13}C NMR Characterization of Nickel(II)-bis(*o*-hydroxynaphthaldimine) Complexes

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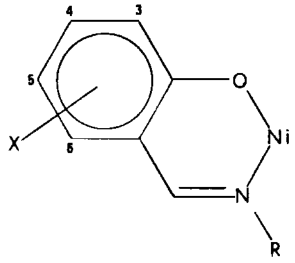
^{13}C NMR spectra of the complexes bis[1-((((*S*)-1-methylpropyl)imino)methyl)-2-naphtholato]nickel(II) (**1**) and bis[1-((((*R*)-1,2,2-trimethylpropyl)imino)methyl)-2-naphtholato]nickel(II) (**2**) have been obtained in mixed solvents (3:1 v/v) $CHClF_2/CDCl_3$ and $CHClF_2/CD_2Cl_2$, respectively, in the temperature range −30 to −100 °C. For **1**, the temperature dependence of the ^{13}C chemical shifts is affected by a shift to the right at lower temperatures of the tetrahedral $\rightleftharpoons$ planar equilibrium. For the largely planar complex **2** ($\mu = 0.55\ \mu_B$), the existence of the following equilibria has been established in solution: umbrella *RR*($\delta\delta$) $\rightleftharpoons$ stepped *RR*($\delta\lambda$) $\rightleftharpoons$ umbrella *RR*($\lambda\lambda$). Two separate signals for the umbrella diastereoisomers are observed at −40 °C from which a molar fraction of 0.94 for the *RR*($\delta\delta$) umbrella form is calculated.

Introduction

Four-coordinate bis-bidentate Schiff base complexes, I, exhibit the equilibria expressed in eq 1[1] in noncoordinating solvents. The



I

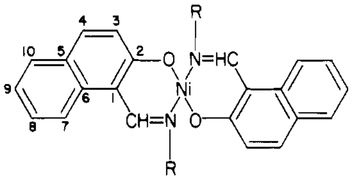
$$\text{polymer(paramagnetic)} \rightleftharpoons \text{monomer(planar diamagnetic)} \rightleftharpoons \text{monomer(tetrahedral paramagnetic)} \quad (1)$$

conformations of chiral complexes of this type, which are of interest in catalysis,[2] have been studied by means of circular dichroism spectroscopy.[3] In the solid state, planar nickel(II) Schiff base complexes have been found in a "stepped" centrosymmetric conformation.[4] Due to the nonplanarity of the chelate rings in solution, two other chiral "umbrella" conformations are possible. (Figure 1). The existence of the equilibrium (2), in which δ and

$$\text{umbrella } (\delta\delta) \rightleftharpoons \text{stepped } (\delta\lambda) \rightleftharpoons \text{umbrella } (\lambda\lambda) \quad (2)$$

λ represent the chirality of the single chelate ring, has been proposed.[3c] The position of the equilibrium (2) depends on the asymmetric induction exerted by the chiral carbon atom of the R substituent (R = chiral group), whose conformational properties are of importance because of the use of such complexes as models for biological systems.[5]

The complexes bis[1-(((S)-1-methylpropyl)imino)methyl)-2-naphtholato]nickel(II) (**1**) and bis[1-((((R)-1,2,2-trimethylpropyl)imino)methyl)-2-naphtholato]nickel(II) (**2**) have been investigated by means of variable-temperature ^{13}C NMR with the hope of understanding their conformational changes in solution.[6]



1 = bis[1-((((*S*)-1-methylpropyl)imino)methyl)-2-naphtholato]nickel(II);
R = $\overset{c}{C}H\overset{d}{C}H_3\overset{b}{C}H_2\overset{a}{C}H_3$
2 = bis[1-((((*R*)-1,2,2-trimethylpropyl)imino)methyl)-2-naphtholato]nickel(II);
R = $\overset{c}{C}H\overset{d}{C}H_3\overset{b}{C}(\overset{a}{C}H_3)_3$

Experimental Section

Preparation of Compounds. 2-Hydroxy-1-naphthaldehyde (Fluka) was purified on a silica gel column, with $CHCl_3$ as eluent. (+)-(*S*)-2-aminobutane (bp 63 °C; $[\alpha]^{25}_D = 7.22°$; optical purity 89%) and (−)-(*R*)-2-amino-3,3-dimethylbutane (bp 100–101 °C; $[\alpha]^{25}_D = -4.9°$; optical purity 76%) were prepared according to the methods reported in literature.[7,8]

Compounds **1** and **2** were synthesized by using previously reported procedures:[1,3c] a higher purity for **2** was obtained by using benzene rather than ethyl alcohol as solvent. A solution of (hydroxynaphthalenecarbaldehydato)nickel(II) (2.5 g) in benzene containing (−)-(*R*)-2-amino-3,3-dimethylbutane (3 cm^3) was refluxed in a flask equipped with a Dean–Stark apparatus for 4 h. The solvent was then removed in vacuo,

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