circumstance makes the present tests more severe than the reported water quenching experiments in DMF.[9] The large H_2O concentration (ca. 20 M) needed to extinguish the emission is expected to modify substantially the environment (as inferred from the spectral changes; cf. Table I); moreover, preferential solvation, favored by hydrogen bonding, may enhance the H_2O content of the second coordination sphere. Since Φ_{CN^-} in H_2O is ca. 50% larger than Φ_{CN^-} in DMF (Table II), its invariance upon addition of water to DMF might result from compensation of some reaction quenching (i.e., the possible contribution of D_1 to the reactivity) with an increment of the CN^- yield.

As a last note, the evidence provided by $Cr(CN)_5(NH_3)^{2-}$ for the quartet as the only, or largely predominant, reaction precursor corroborates previous interpretations with other chromium(III) am(m)ine complexes where LF excitation gives rise to two[19,58b,67,68] or even three[21] different products. The following features are common to all these systems: (1) BISC is possible on energetic grounds; (2) the photoreactivity can be partially quenched; (3) the proportion of the various modes is the same for the quenchable and unquenchable photochemistry.

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Photoinduced Electron Transfer by Coordination Chemical Pathways across Pyrite/Electrolyte Interfaces

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Experiments are presented which show that, in the case of pyrite (FeS_2), interfacial transition-metal bridge complexes formed by attaching –O–, –CN–, or –CO– groups facilitate electronic charge transfer more efficiently by inner-sphere mechanisms (strong interaction) than may occur by tunneling (weak interaction). This is advantageous concerning electrode stability and catalytic activity. The described experiments also show that appropriate chemical surface modifications can channel photogenerated charge carriers through the interface of d-character materials at a high photocurrent density ($\sim$30 mA cm^{-2}) and with good stability. Individual –CN– groups attached to the FeS_2 interface pass photogenerated charge carriers at least 10^6 times before a side reaction occurs. New models have to be developed to describe the semiconductor/electrolyte interface in cases with strong chemical interaction. A first qualitative picture is presented.

Introduction

Semiconductors possessing valence bands with pronounced d character like MoS_2, RuS_2, and FeS_2 have proved to be reasonably efficient in converting light to electricity and fuels in electrochemical solar cells.[1,2] In addition, semiconducting materials containing transition-metal clusters have been shown to be catalytically active particularly for multielectron transfer reactions.[3,4] A proposed explanation for these favorable properties is the involvement of interfacial coordination chemistry. To substantiate the importance of chemical interaction at the semiconductor/electrolyte interface during electron transfer processes, a FeS_2 photoelectrode in contact with an Fe^{2+} containing electrolyte has been selected as a model system. As a semiconductor, FeS_2 is still a poorly explored material for which neither the stoichiometry nor the doping has yet been optimized. The synthetic samples used (grown by vapor transport) have a sulfur deficit[5] (most likely Fe_2S_3) causing a defect concentration of approximately 10^{20} cm^{-3}. These defects give rise to energy levels within the forbidden energy gap, which are probably responsible for the small photopotential (200 mV) but do not affect the very large quantum efficiency (80–90%) observed in the presence of appropriate electron donors (I^-, Br^-, $Fe(CN)_6^{4-}$). Previous experiments with FeS_2 have shown that the positively charged Fe^{2+} ion is an inefficient electron donor at the illuminated pyrite surface.[6] This has been interpreted as being caused by the ion's inability to interact with the interfacial iron states, where photogenerated holes are available for reaction.[2,6]

To facilitate coordination chemical transfer of holes from Fe states in the FeS_2 interface to Fe^{2+} ions in the electrolyte (which can only exchange electrons by tunneling), various bridge complexes can be made by introducing the appropriate ligand (=O, =CO, =CN) to the pyrite/electrolyte interface. The experimental aim of this work was to explore the advantage of such bridges for interfacial photoinduced electron transfer.

The theory of photoelectrochemical kinetics started with Gärtner's model,[7] and during the following 20 years scientists focused their attention mainly on the semiconductor part of the interface, describing physical properties such as charge separation, transport, and recombination within the solid-state phase.[8,9] In the presence of a sufficiently high concentration of the redox species and adequate mass transport conditions, interfacial electron transfer, assumed to occur via tunneling processes, typically appeared not to be rate limiting.[10,11] Lately, with the exploration of Fermi level pinning[12,13] and with kinetic suppression of corrosion via d-state photoelectrochemical reactions,[1] it became obvious that for some systems interfacial electron transfer is as important for the overall performance of the photoelectrode as semiconductor bulk properties. Classical theoretical models including interfacial reactions of a semiconductor with a redox couple in solution are based on quantum-mechanical tunneling, assuming weak interaction between the semiconductor and the redox couples in so-

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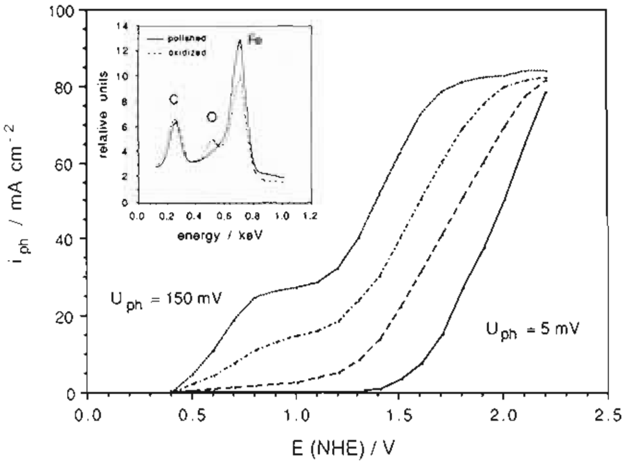

Figure 1. Photocurrent–voltage characteristics of n-FeS_2 in 0.5 M $FeSO_4$ (pH 2–3) after different oxidation times (light intensity ~280 mW cm^{-2}, anodic sweep rate 25 mV/s): (1) pure surface after polishing (solid); (2) partially oxidized surface (dashed and dashed-dotted); (3) completely oxidized surface (dotted). Insert: X-ray fluorescence measurements (exitation energy: 2.3 keV) indicating formation of oxide layers on electrochemically oxidized pyrite surfaces.

lution. Unsolved problems have been pointed out by various authors, e.g. Khan and Bockris.[14]

The present work aims at experimental evidence in support of strong chemical interaction during interfacial electron transfer and at the demonstration of its advantage for photoelectrochemical energy conversion.

Experimental Section

The preparation and the structure of n-type FeS_2 single crystals have been described in literature.[15] These crystals were mounted onto a copper rod with silver epoxy, encapsulated with epoxy resin (Scotch cast 3 M XR 5241), and polished with diamond pastes with successively decreasing grain size (3–0.25 μm). A standard photoelectrochemical setup was used for current–voltage measurements (potentiostat Bank POS 73, lock-in PAR 5204, chopper PAR 9479, light source Oriel W-Hal 250 W, X-Y recorder Rhode & Schwarz ZS K2). RRDE measurements were performed by using Pine instruments (RDE 3 bipotentiostat, MSR speed control) and a PM 8132 XY1Y2 recorder (Philips). The purity of the chemicals was of analytical grade, and all soltions were purged with nitrogen gas for more than 20 min before starting the experiments. A calomel electrode was used as reference. All potentials are given with respect to the NHE.

Results

Effect of Oxidation. After polishing (no etching) of the pyrite surface, there are a very small photocurrent and a relatively high dark current for the Fe^{2+} oxidation in 0.5 M $FeSO_4$ (pH 2–3, no buffer) (cf. Figures 1 (solid line), 3, and 6). During the sweep in the noncorrosive region (0.1–0.8 V (NHE)), the dark current decreases quite rapidly while the photocurrent remains largely constant (cf. Figures 4 and 7). The high dark current at the beginning and its decrease can be explained in terms of oxidizable FeS centers near the surface (Figure 8). After one sweep (5 mV/s) up to 2.2 V (NHE), the surface is partially oxidized and the photocurrent of the Fe^{2+} oxidation increases as shown in Figure 1 (dashed lines). When the potential is held about 5 min at 2.0 V (NHE), the surface is totally oxidized (black; cf. insert of Figure 1) and the photocurrent for the Fe^{2+} oxidation again increases (cf. Figure 1 (dotted line)). This increase in photocurrent (more than 200 times) is accompanied by an increase in photovoltage (30 times), as indicated in Figures 1 and 2.

At potentials more positive than 1.0 V (NHE), the light-produced holes have two possible reaction pathways via the valence band: (1) oxidation of Fe^{2+}; (2) corrosion of FeS_2 forming FeO_x, Fe^{3+}, and SO_4^{2-}. Smaller light intensities lead to a lower percentage of corrosion (cf. Figures 2 and 3); e.g., all light-produced holes first oxidize Fe^{2+}, and only if there are not enough Fe^{2+} ions near the interface, will the presence of holes lead to corrosion. The effect of agitation (arrow in Figure 2) confirms this diffusion limitation of the Fe^{2+} oxidation.

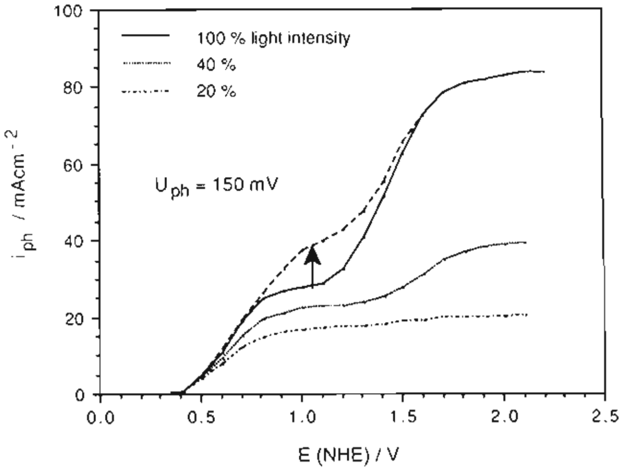

Figure 2. Photocurrent–voltage characteristics of n-FeS_2 in 0.5 M $FeSO_4$ (pH 2–3) after complete oxidation and different light intensities (100%, ~280 mW cm^{-2}) (anodic sweep rate 25 mV/s). The arrow indicates the effect of agitation (100% light intensity).

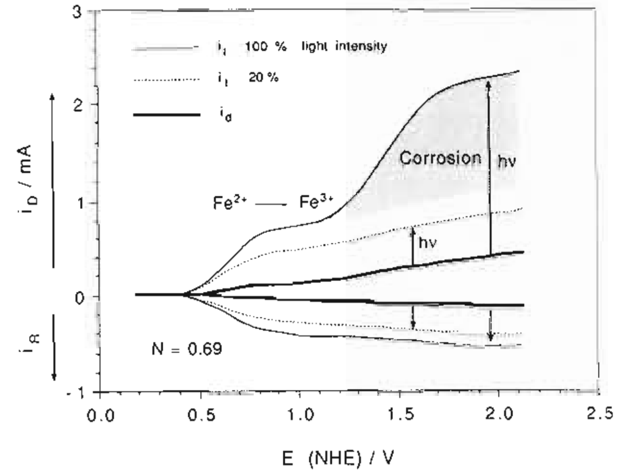

Figure 3. I_D–E_D and I_R–E_D curves for an n-FeS_2 (disk)–Pt (ring) electrode in 0.5 M $FeSO_4$ after formation of an oxide layer (E_R = 0.25 V (NHE), E_D scan rate 5 mV/s, rotation speed 400 rpm, light intensity ~280 mW cm^{-2}). The corrosion region is shaded.

X-ray fluorescence analysis (insert of Figure 1) gives an approximate value of 1000 Å for the integral thickness of the oxide layer. It is not yet clear whether the whole pyrite surface is covered with a uniform oxide layer or simply whether a high roughness of the surface leads to such a high value. In both cases the surface is covered with a porous oxide layer, which still allows the electrolyte to reach the pyrite junction. Bridge type complexes can be formed with the iron in the solution. We assume two oxide bridges, because many stable examples are known in the literature.[16]

Because of these uncertainties with oxide layers, we sought other systems forming better defined interfacial bridge structures.

CN^- Treatment. After a pyrite electrode is polished (no etching) and immersed in ~0.5 M KCN for about 1 min, the photocurrent and the photovoltage increase (Figure 4 (curve 3)). The photocurrent changes with time (30 min) may be due to a quite small amount of Fe–CN centers at the polished pyrite surface, which may undergo transformation or side reactions. More important is that the dark current increases drastically (Figure 7 (curve 3)) and remains stable over a period of several hours.

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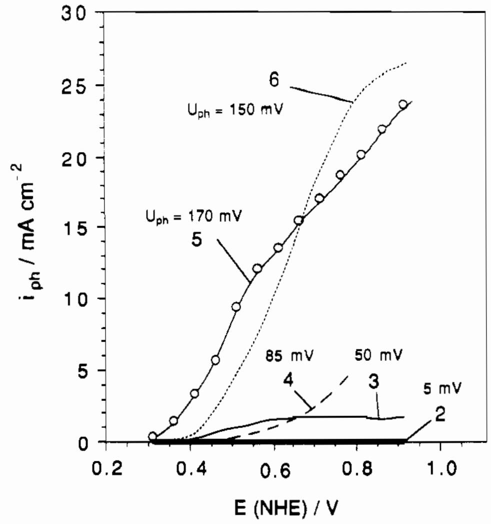

Figure 4. Photocurrent-voltage characteristics of n-FeS_2 in 0.5 M $FeSO_4$ (pH 2-3) after different treatments (anodic sweep rate 25 mV/s, light intensity ~280 mW cm^{-2}). The numbers have the same meaning as in Figure 7.

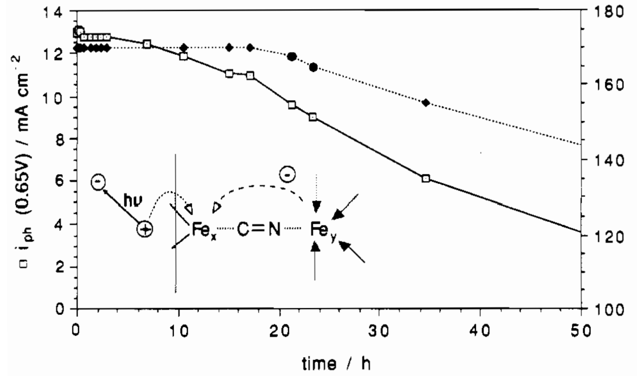

Figure 5. Photocurrent (solid) and photopotential (dashed) versus time for n-FeS_2 in 0.5 M $FeSO_4$ (pH 2-3) after polishing, H_2 evolution treatment for 30 min in 0.5 M H_2SO_4, and immersion for 1 min in ~0.5 M KCN (pH 13). The inserted scheme shows the electron transfer via the -CN- bridges (for more details see Figure 9).

After polishing and H_2 evolution treatment for 30 min in 0.5 M H_2SO_4, the dark current (Figure 7) and the photocurrent and the photopotential increase (Figure 4), but after the electrode is immersed for 1 min in ~0.5 M KCN, all these values further increase drastically (Figure 4).

This combined treatment leads to high stationary photopotentials (170 mV). The dynamic photopotentials obtained directly from the current-voltage curves are around 270 mV.

The stability of such an interface is very good due to the catalytic function of the proposed Fe(pyrite)-CN layer at the surface. Less than 10% decay in photocurrent is found after sweeping (0.2-0.65 V (NHE)) for more than 10 h (Figure 5), with a total photocharge passed of ~140 C cm^{-2}.

Assuming 10^{15} Fe centers/cm^2 and one CN^-/Fe center, a charge of 0.16 mC cm^{-2} is passed when one electron is transferred via the bridges; thus, we can estimate the ratio between the electron transfer without ligand transfer and the electron transfer accompanied by ligand transfer (which leads to corrosion of the pyrite -Fe-CN bridge-centers) as $>10^6$.

In the case of illuminated pyrite we have one Fe^{3+} center at the pyrite surface and one Fe^{2+} center in the solution. In combination with cyanide, it is reasonable that a structure with one bridging cyanide bond with the C side to the pyrite (stronger bonding) and with the N side to the iron in the solution is formed, as in the very stable and well-known complex Prussian Blue: $[Fe^{III}Fe^{II}(CN)_6]^-$.[17] In the case where the two iron centers have the same valency (e.g. 3+ after the electron is transferred), even more stable complexes with a bridging cyanide of the type M-CN-M are known.[18]

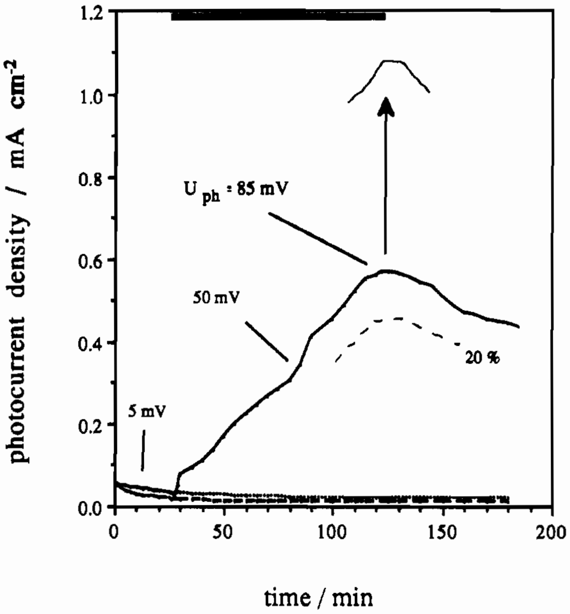

Figure 6. Photocurrent versus time for n-FeS_2 in acetonitrile/0.1 M TBAP (potential held at 0.7 V (MSE)): (dotted) N_2 and $FeSO_4$ saturated; (solid) CO and $FeSO_4$ saturated; (dashed) CO saturated. For the last two curves the black bar indicates the time of CO bubbling. The arrow indicates the effect of agitation (100% light intensity ~280 mW cm^{-2}).

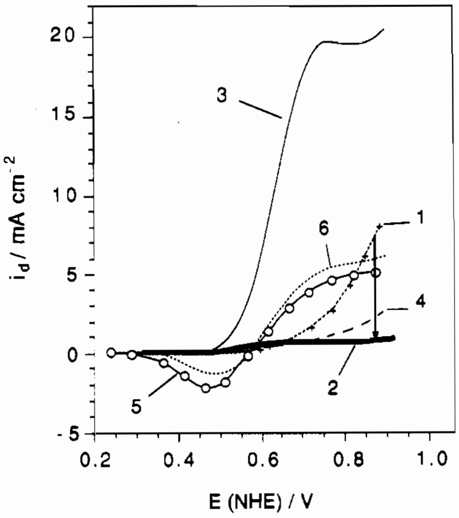

Figure 7. Dark current-voltage characteristics of n-FeS_2 in 0.5 M $FeSO_4$ (pH 2-3) (obtained from chopped light current-voltage curves) after different treatments (anodic sweep rate 25 mV/s, light intensity ~280 mW cm^{-2}): (1) after polishing; (2) after polishing and 30 min of sweeping (0.2-0.8 V (NNHE)); (3) after immersing for 1 min in ~0.5 M KCN (pH 13) and rinsing with H_2O; (4) after H_2 evolution treatment for 30 min in 0.5 M H_2SO_4; (5) after treatments 4 and then 3; (6) after anodic formation of an oxide layer.

In order to provide direct evidence that cyanide is coordinated to the semiconductor surface, FTIR experiments with a pressed pellet were performed, but have not yielded conclusive results so far. One problem is that the hydrogen treatment for loosly packed pellets if different from the single-crystal electrochemical experiments. On the other hand, we could not use pyrite single crystals as in the electrochemical experiments, since the surface of our crystals is too small to get significant signals. IR studies on thin layers of pyrite using multiple reflection are in progress.

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CO Treatment. To verify that the improvement of the interfacial electron transfer due to cyanide treatment is not a single case, but justifies some general conclusions, we have chosen CO as a second example. Although the chemistry of CO as a ligand is very different from the chemistry of CN as a ligand, both are among the strongest ligators to transition metals. Since the polished pyrite surface is not very reactive, we needed either strong ligands or iron-selective ligands to see this effect. One example of an iron-selective and well-known inner-sphere bridging ligand is the chloride ion. In a previous article,[2] we demonstrated the enhancement of the photocurrent via Cl bridges.

Upon adding CO as bridge ligand to organic electrolytes, saturated with $FeSO_4$ (<1 mmol), we also find a significant increase in the photocurrent and photopotential of FeS_2, (cf. Figure 6). The increase in these values is comparatively slow, because the neutral CO cannot react as efficiently as the negative CN^- with the pyrite surface. The process of Fe^{2+} oxidation with this system is also limited by diffusion of the Fe^{2+} ions: note the effect of agitation (arrow in Figure 6) and the very small difference in current response for 100% and 20% light intensity. The effect of agitation is even more obvious when organic electrolytes are used, because of the much lower concentration of Fe^{2+}.

Further experiments are necessary to decide whether one or two CO bridges are active per Fe center. We are inclined to assume two bridges, because in the literature many stable complexes with two CO bridges between two iron centers forming a ring current are known.[19]

Discussion

Evidence for Improvement of the Electron Transfer. Besides selective etching of damaged pyrite surface sites (which we do not consider an important process, since dark currents do not decrease as a consequence of cyanide treatment), there are two possible explanations for the observed increase in photocurrent and photopotential: (1) the sulfur deficiencies, with 1 equiv to dangling Fe bonds, are occupied by partly negatively charged ions like cyanide, which neutralize recombination centers; (2) the electron transfer from $Fe(H_2O)_6^{2+}$ in solution to the Fe^{2+} in the pyrite is significantly favored via chemical bridges at the interface as compared to tunneling.

If the first explanation is correct, then a modification with cyanide should not affect the dark current, but in the second case, the dark current should increase, provided there are energy levels that facilitate electron transfer in the dark.

After a pyrite electrode is polished (no etching) and immersed in ~0.5 M KCN for about 1 min, the dark current resulting from the Fe^{2+} oxidation (confirmed with RRDE measurements) drastically increases (Figure 7). When hydrogen is first evolved and the electrode is then immersed in KCN, the increase of the Fe^{2+} oxidation in the dark is less pronounced, because it is more difficult for the electrons to reach the conduction band after the electron transfer when the high impurity level concentration (10^{20} cm^{-3}) within the band gap is reduced.

One effect of the hydrogen evolution treatment is probably to saturate the dangling bonds of the impurity centers, forming FeSH. As a result, these no longer act as recombination centers and electron-acceptor levels within the barrier.[5] Therefore the hydrogen treatment should increase the tunnel probability through the barrier. In the case of 1 M KI (pH 1), the effect of the hydrogen treatment is approximately a doubling of the photocurrent. After hydrogen treatment, the quantum efficiency reaches 90%, but when 0.5 M $FeSO_4$ (pH 2–3) is the electrolyte, the quantum efficiency after hydrogen treatment, although improved, is still very small. On the one hand, it is known that halogen species interact strongly with positive iron centers.[25a,22] It has been shown in recent ion-scattering experiments[20] that bromide is adsorbed onto Fe centers in the pyrite surface without reacting chemically. On the other hand, Fe^{2+} ions cannot bind directly to these iron centers in pyrite, but with a mediating bridge it would be possible. This is demonstrated by the drastic increase in photocurrent after CN treatment (see Figure 4).

Table I. Effect of Different Treatments on Photocurrent and Photovoltage[a]

polished	cathodic polarizn	KCN treatment	kinetic	FeS	I_{ph}/I_d	$I_{ph} + I_d$, mA cm^{-2}	U_{ph}, mV
*			–	–	<0.1	<1	5
*	*		–	+	~3	~3	85
*		*	+	–	<0.1	21	50
*	*	*	+	+	~4	23	170

[a] For the first row we have used values after stabilization; a plus in the column "FeS" means a low concentration of defects. See text.

Another indication that the second explanation is correct can be deduced from experiments with outer-sphere electron donors, which are not able to form chemical bonds with the attached cyanide at the surface. Hence, their photocurrents should not be affected by the cyanide treatment. Indeed, we observe no change in the photocurrent after CN^- treatment when using a 0.1 M $Ru(NH_3)_6^{2+}$ solution as electrolyte. In the case of ~0.1 M ferrocene in acetonitrile (0.1 M TBAP), the photocurrent is decreases after the CN^- treatment, which can tentatively be explained in terms of longer tunnel distances. Detailed studies with outer-sphere electron donors are in progress.

Further experiments have shown that the enhancement of the photocurrent is strongly dependent on the surface orientation: Whereas Fe(100) contributes a strong effect, Fe(111) shows no significant effect.[21] This difference is another indication of coordination chemistry on the surface.

Recent temperature dependence measurements also indicate that coordination chemistry is involved with the introduction of CN bridges.[22]

Altogether, bridging ligands drastically increase the flow of electrons through the pyrite/electrolyte interface ($I_{ph} + I_d$ in Table I), whereas the cathodic polarization determines the direction of this current (I_{ph}/I_d in Table I): either via the conduction band (prior to polarization) or via the valence band (after polarization). The electrons from the iron centers in the solution must first cross the interface and then the semiconductor without recombination to generate a net current flow. Obviously, the bridge formation is correlated with the first step ("kinetic" in Table I) and the polarization with the second step ("FeS" in Table I); see also next paragraph.

Theoretical Models. Figure 8 depicts an electron energy scheme describing interfacial electron transfer via the tunneling processes based on weak interaction, as frequently discussed in the photoelectrochemical literature.[10,11,23] Since Fe^{2+} cannot chemically interact directly with positively charged iron centers in the pyrite interface, this scheme adequately describes the situation during photooxidation of Fe^{2+} directly after polishing the crystals (Figure 8a), which is characterized by very poor efficiency (cf. Figure 1). After KCN treatment (Figure 8b), the dangling bonds should be reduced or neutralized. Consequently, we would expect a lower dark current and a higher photocurrent. In fact, the recombination of light-produced holes is still very high and the dark current increases drastically. After cathodic polarization (Figure 8c), we find the same discrepancies. But if we use KI as electrolyte, we find the expected behavior: high photocurrent and low dark current after cathodic polarization (see Figure 8d). Figure 8d is also obtained after the combined H_2/KCN treatment. As pointed out earlier,[1-3] these schemes cannot describe the large difference in photooxidation of positively charged (Fe^{2+}, Mn^{2+}) and negatively charged electron donors like I^-, Br^-, and $Fe(CN)_6^{4-}$, which are able to attach themselves to transition-metal sites in the interface. Strong interaction mechanisms (adiabatic electron transfer) must be involved, which is confirmed by the increase in electron transfer rates upon attachment of chemical bridges

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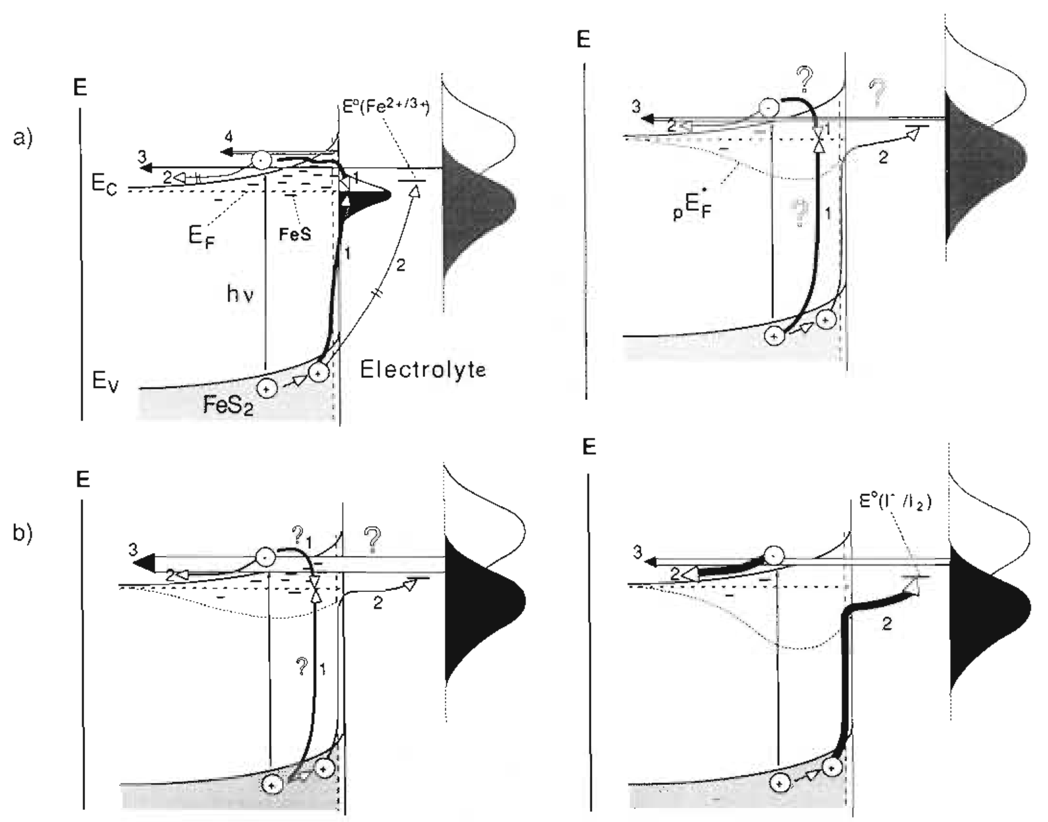

Figure 8. Electron energy scheme of the illuminated pyrite/$FeSO_4$ interface with different reaction pathways for the charge carriers: (1) recombination via surface states; (2) photooxidation of Fe^{2+}; (3) dark oxidation of Fe^{2+}; (4) dark oxidation of impurity centers at the surface. Diagrams: (A) directly after polishing; (B) after KCN treatment; (C) after cathodic polarization. Part D: the pyrite/1 M KI interface after cathodic polarization.

that facilitate electron transfer.

At the end of this paragraph we present an idea to modify the existing energy schemes in order to describe strong interaction mechanisms. A combined electron energy (E)-total energy (U) diagram explaining the transfer of photogenerated electronic charge carriers via ligands (-CN-, -O-, -CO-) attached to interfacial transition metals and able to form electron-transfer bridges to dissolved ionic transition-metal electron donors is shown in Figure 9 in a simplified way. The strong chemical interaction, as exhibited by the bridge type complexes, leads to repulsion terms that permit electron transfer on a smooth potential energy surface, described as an adiabatic transition (nonintersecting electron terms), shown as solid line through positions 2 and 3. In Figure 9, the splitting of the electron terms is clearly demonstrated. It was necessary to draw a three-dimensional picture,[10b,24] because two coordinates besides U vary when an $Fe(H_2O)_6^{2+}$ ion is transferred from the bulk of the solution (Fe_z, circle 1) to the bridge position (Fe_y, circle 2): the distance R and the solvation coordinate q. In accordance with electron-transfer theory,[25,26] the electron transfer occurs at q^*, leading to an oxidized Fe_y^{3+} at position 3, which now undergoes ligand substitution with water and disappears as $Fe(H_2O)_6^{3+}$ (position 4). At the same time that the electron is transferred[27] at q^* to Fe_x, a photogenerated hole recombines with this electron and Fe_x is again oxidized. This process is much faster than the chemical reactions at the surface (Figures 2 and 3). In Figure 9 are depicted the qualitative values for U referring to one oxidation cycle without the external light-produced holes. Because the rate constants for Fe^{2+} substitution reactions with cyanide is approximately 100 time higher than for substitution reactions with Fe^{3+},[28] the rate-limiting step should be either the electron transfer (from position 2 to 3) or the back-transport of the oxidized ion from position 3 to 4. Taking

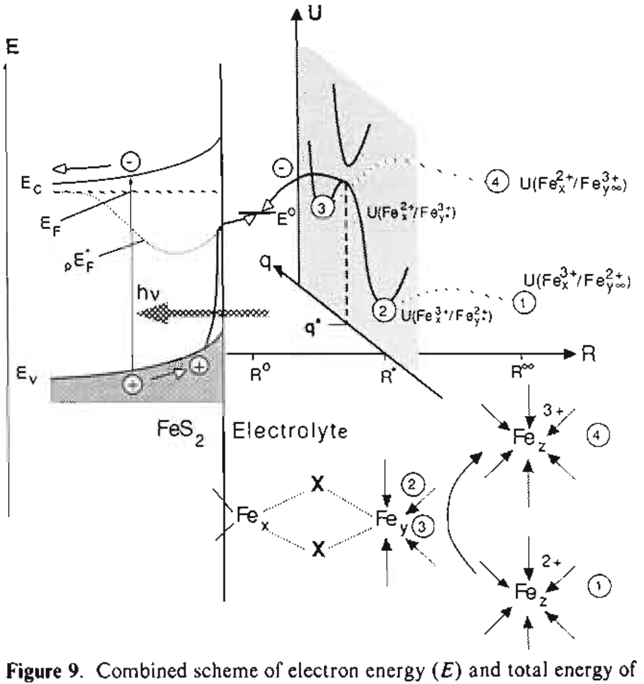

Figure 9. Combined scheme of electron energy (E) and total energy of the system (electrons + ions + solvent) (U) of the illuminated pyrite/$FeSO_4$ interface. Fe_x at R^0 belongs to the pyrite surface, and Fe_z at R^∞, to the bulk of the solution. The electron transfer is only possible at q^* and R^* with the Fe^{2+} at position y. X stands for the different bridge ligands. In case of -CN-, only one bridge is formed. For more details, see text.

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into account the increase in the photocurrent while stirring the solution, we conclude that the back-transport is the rate-limiting step. In order to calculate a system like the one briefly described above, it may be possible to combine the unified model of the adiabatic reactions of electron transfer at metal electrodes from Kuznetsov,[24] based on the DKV model[29] with conventional equations for photoelectrodes.[9]

In all cases in which it is possible to form stable bridge type complexes at the semiconductor interface, we have in principle the chance to move the transition from electronic to ionic conduction (which is linked with the risk of recombination and corrosion) from the solid-state interface into the solution, which can in addition imply better conditions for catalysis of energy conversion processes. This provides access to a wide range of interesting surface chemistry with a corresponding variety of kinetic mechanisms. Many examples in the literature are already known of modified semiconductor interfaces. Most of them are also based on strong chemical interactions,[30-33] but mainly those between the reacting species and the surface-modifying chemical species. They do not however emphasize the exchange of electronic charges with the semiconductor electrode. In these cases, only part of the electron or hole path is supported by strong chemical interaction. High photocurrent densities (e.g. 30 mA cm^{-2}) in combination with high stability (Figure 5), as in our experiment, have not yet been obtained.[34] It appears to be advantageous to provide charge carriers for interfacial photoelectrochemical reactions via unbroken chemical bonds instead of attempting to transfer charge carriers from broken chemical bonds to transition-metal complexes attached to the surface.[34] Moreover, a door is opened to a large variety of modifications involving different chemical reactions with the bridges themselves.

We think that related transition-metal compounds can be modified chemically in an analogous way and that such strong interfacial electron-transfer mechanisms promise interesting opportunities for photoelectrochemical energy conversion. Pyrite with its interfacial coordination chemistry and its d-band structure is a good example of a compound displaying strong interfacial interaction, whereas GaAs in contact with acetonitrile is a good example of one exhibiting weak interaction and tunneling processes. Many other systems lie between these, and electron transfer is dependent on the special nature of the chemistry involved. The behavior of such systems can only be described by combination of the two extreme models.

Better theoretical knowledge of electron-transfer processes with strong chemical interaction at the semiconductor/electrolyte interface would be very helpful in developing ideas to chemically modify each individual system in the most effective way.

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Electron Delocalization in Molecule-Bridged Polymetallic Systems. Unique Neutral Complexes of TCNE or TCNQ and up to Four Organometallic Fragments $(C_5R_5)(CO)_2Mn$

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Electron transfer between the π-accepting TCNE or TCNQ (TCNX) ligands and π-electron-rich organometallic species $(C_5R_5)(CO)_2Mn(THF)$ (R = H, CH_3) results in the formation of polynuclear complexes $[(C_5R_5)(CO)_2Mn]_n(\eta^n\text{-TCNX})$ until full coordinative saturation is achieved at the nitrile groups ($n = 4$). Infrared spectroscopy points to the net transfer of one π electron to the TCNX acceptor ligand and indicates a highly symmetrical and strongly coupled situation for the tetranuclear complexes. The polynuclear complexes have intense ($\log \epsilon > 4.3$) absorption bands in the near-infrared region (0.8–1.5 μm), and the corresponding transitions may be formulated either as metal-to-metal ($Mn^I \rightarrow Mn^{II}$) charge transfer in a localized, mixed-valence formulation or as $\pi \rightarrow \pi^*$ transitions of polymetal-containing π systems in a delocalized description. The polynuclear systems may serve as models for the MLCT excited states of symmetrical dimers and tetramers. Results from Hückel molecular orbital calculations involving $d(\pi)$–$p(\pi)$ bonding correlate with the changes in absorption energies on successive polynucleation. The small energy differences between frontier orbitals are confirmed by results from cyclic voltammetry. As an additional complication, the complexes contain metal centers that possess an easily attainable intermediate-spin state ($S = 1$) despite their 18-valence-electron configuration.

Coordination compounds with considerable metal/ligand delocalization have been known e.g. in the form of the dithiolene chelate complexes;[1] several special features make such compounds very interesting also for practical purposes: (i) Intense charge-transfer absorption bands in the visible and in the near-infrared region can make such systems useful as dyes for information storage using fiber optics and 1.0–1.6 μm diode lasers,[2] (ii) the communication between metal-connected ligands and/or ligand-connected metals has received attention in the area of low-dimensional polymers with electron-propagating capabilities and

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