Work is in progress to establish the generality of this reaction for use in organic synthesis. Thus, it is observed that a facile reaction also occurs with compounds containing a single α hydrogen, although it has not yet been possible to isolate the major reaction products. Previous studies have demonstrated that aldehydes and ketones with no α hydrogens undergo an entirely different (and much slower) reaction involving the ammonia ligand trans to the nitrosyl group.[18]

The most apparent synthetic potential of reactions 1 and 2 is for oxidative ring opening and bifunctionalization of cyclic ketones under very mild conditions, thus representing an excellent alternative to present oxidative cleavage methods such as Marshall's[19] cleavage of α-diketone monothioketals or the known oxidative cleavage of cyclic olefins[20] for the synthesis of macrocyclic compounds or compounds containing linear chains with fixed stereochemistry.

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(15) Support for this mechanism is provided by (a) the isolation of oximes in many of the analogous nitroprusside reactions[14] and (b) our observation of the formation of a nitrile ruthenium species in the reaction of $(H_3N)_5RuOH_2^{2+}$ with diacetyl monoxime, presumably by the reaction sequence $(H_3N)_5RuOH_2^{2+} \rightarrow (H_3N)_5RuN(OH){=}C(CH_3)C(O)CH_3^{2+} \rightarrow (H_3N)_5RuN{\equiv}CCH_3^{2+}$ + other products.
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Luminescent Photoelectrochemical Cells. Use of Tellurium-Doped Cadmium Sulfide Photoelectrodes to Probe Surface Recombination during the Conversion of Optical Energy to Electricity

Sir:

Photoelectrochemical cells (PECs) consisting of an illuminated n-type semiconductor photoelectrode, a Pt counterelectrode, and a suitably chosen electrolyte have been used to convert optical energy directly into electricity.[1-8] Improvement of PEC efficiencies requires an understanding of the excited-state properties of semiconductor electrodes and, in particular, the extent to which they can be manipulated by experimental parameters. Thus far, attention has focussed on *nonradiative* deactivation leading to electrochemistry and, more specifically, on the role of the electrolyte in determining whether oxidation of the electrode and/or the electrolyte occurs.[1-9] Studies of *radiative* deactivation involving semiconductor electrodes have been largely confined to transient electroluminescent phenomena.[10,11]

We now report that PECs employing n-type, Te-doped CdS (CdS:Te) photoanodes provide a sensitive probe of the manner in which the semiconductor excited state partitions input optical energy. Photoelectrochemical events are presumed to result from separation of a photogenerated conduction band electron and valence band hole, a consequence of the band bending which characterizes the depletion region created by the semiconductor-electrolyte interface.[12] *The observation of emission in an operating PEC signifies that radiative recombination of electron-hole pairs occurs in direct competition with nonradiative separation leading to electrochemistry.* We demonstrate herein that this competition is sensitive to a PEC parameter which affects band bending, the electrode potential.

Vapor-grown, n-type CdS:Te single crystals are well characterized and are known to luminesce at room temperature upon ultraband gap excitation;[13] the band gap of CdS:Te is at most that of undoped CdS, 2.4 eV.[14] Samples of melt-grown, polycrystalline CdS:Te (5–100 ppm Te) used in this study were etched in concentrated HCl prior to use and exhibit both orange emission (band maximum ~600 nm) and photocurrent at 298 K upon excitation at $\lambda \lesssim 520$ nm.[15] The emission has been ascribed to radiative recombination of excitons trapped at Te atoms which presumably substitute at S sites.[13]

In order to study CdS:Te emissive properties in the PEC, the cell was assembled in the compartment of a spectrophotofluorometer. A 3-mm-diameter Ar ion laser beam was used to excite CdS:Te electrodes positioned at ~45° to both the incident beam and the emission detection optics. Excitation anywhere on the CdS:Te surface causes the entire electrode to emit, since emitted light is not appreciably absorbed by CdS:Te. A Pt foil counterelectrode, an SCE, and electrolytes of sulfide (1 M OH^-/1 M S^{2-}) or polysulfide (1 M OH^-/1 M S^{2-}/0.2–1.0 M S) complete the PEC whose electrochemistry is essentially that of undoped CdS-based PECs.[1-5] That is, oxidation of (poly)sulfide electrolytes competitively precludes the photoanodic decomposition reaction

$$CdS \xrightarrow{h\nu} Cd^{2+} + S + 2e^- \qquad (1)$$

observed in OH^- electrolyte. Reduction of polysulfide species at Pt permits sustained optical to electrical energy conversion, since no net change in electrode or electrolyte composition occurs. We observe minimal weight loss or surface damage for CdS:Te even when sufficient photocurrent is passed to have yielded measurable decomposition.[16] Under sustained PEC operation the emission spectrum is unaltered, although we do see both declining photocurrent (similar to that reported for the undoped CdS[1,2]) and emission intensity.

But for intensity differences, the emission spectrum of the CdS:Te electrode from 540 to 800 nm (bandwidth 5 nm) is independent of Ar ion excitation wavelengths (457.9 to 514.5 nm), electrode potential (−0.1 V vs. SCE to the onset of cathodic current),[17] and the composition or presence of (poly)sulfide electrolytes. The crucial result is presented in Figure 1 for 488.0-nm excitation. Increasingly negative bias, corresponding to diminishing band bending within the depletion region, is shown to increase luminescence by up to ~40% as the photocurrent declines to zero. The same effect is noted in sweeping this potential region; we observe that 10 consecutive scans at 100 mV/s are reproducible to within 5%. Excitation at 457.9, 488.0, and 501.7 nm in (poly)sulfide electrolytes

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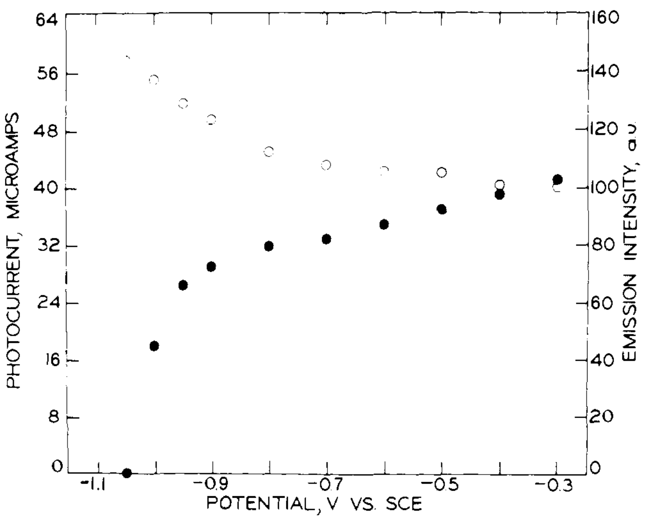

Figure 1. Emission intensity (right-hand scale and ○) monitored at 600 nm and photocurrent (left-hand scale and ●) for a 5-ppm CdS:Te-based PEC employing unstirred 1 M OH^-/1 M S^{2-}/0.2 M S electrolyte. The polysulfide electrolyte redox potential is at −0.72 V vs. SCE so that optical to electrical energy conversion obtains at voltages more negative than this value. The 10 × 10 × 3 mm photoelectrode was excited with 5 mW in an ~3-mm-diameter beam (~70 mW/cm^2) of 488-nm light; this intensity has been corrected for solution absorbance. Quantum yields for electron flow in the external circuit may be determined by dividing the photocurrent values by 2000.

yields similar intensity increases, generally 20–80%. However, emission from irradiation at 514.5 nm on the band gap edge is expected and observed to be less sensitive to electrode potential, since a much smaller fraction of incident light is absorbed within the depletion region.[18] Under the conditions of Figure 1, excitation at 514.5 nm yields substantially reduced photocurrents and <6% variation in the emission intensity over the same potential range. As with other PECs, optical to electrical energy conversion occurs at potentials more negative than ~−0.7 V vs. SCE, the polysulfide redox potential.[1,2]

Although it is intriguing to speculate that radiative deactivation might increase directly at the expense of the nonradiative deactivation route represented by photocurrent, a complete energy balance including the predominant nonelectrochemical, nonradiative decay route is required to determine the extent to which such a trade-off occurs. We estimate the best optical to electrical conversion efficiencies to be ~0.6%, corresponding to an output voltage of 0.23 V and a quantum efficiency for electron flow in the external circuit of 0.06 from an input power of 1.3 mW (18.2 mW/cm^2) at 488.0 nm. A reasonable upper limit of emission quantum efficiency is 0.025, based on our observation that the 77 K CdS:Te emission spectrum is ~40 times the 298 K intensity. Measurements with a flat-response radiometer of the back surface emission off CdS:Te electrodes indicate that conversion to emission can be as large as 0.1–1.0%. We should point out that the efficiencies reported here for CdS:Te-based PECs have not been optimized and that several other PEC parameters including electrolyte and temperature can be expected to influence efficiency. A detailed characterization of the CdS:Te-based PEC is in progress and will be reported in the full paper.

Note Added in Proof. The use of Br_2/MeOH as an etchant results in substantially improved optical to electrical energy conversion efficiencies of 3–5% with 500-nm excitation. The luminescent properties described above are preserved with this etchant.

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(16) Starting weight, 1.9750 g; final weight, 1.9749 g. CdS:Te (100 ppm) was photolyzed with a UV-filtered 200-W Hg lamp for 210 h at an average photocurrent of 0.066 mA in 1 M OH^-/1 M S^{2-}/0.2 M S at −0.05 V vs. a Pt counterelectrode. The expected weight loss (eq 1) is 0.0373 g.
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Potential Proximate Carcinogens of 7,12-Dimethylbenz[*a*]anthracene: Characterization of Two Metabolically Formed *trans*-3,4-Dihydrodiols

Sir:

7,12-Dimethylbenz[*a*]anthracene (**1**) is one of the most potent carcinogenic polycyclic aromatic hydrocarbons known, and is much more potent than the more extensively studied carcinogen, benzo[*a*]pyrene.[1,2] Metabolic activation by mammalian drug-metabolizing enzyme systems is required for the biological properties exhibited by **1**.[2] Enzymatic hydroxylation at the 7-methyl group yields 7-hydroxymethyl-12-methylbenz[*a*]anthracene (**2**) which has higher adrenocorticolytic activity[3] and has similar or reduced carcinogenicity[3,4] in comparison with those of **1**. It has been suggested[5]