mp 125-131 °C (NMR δ 5.87, dd, J = 2.2 and 0.5 Hz, 4-H; 1.15, s, H-19; 0.83, s, 18-H) as a minor product (18% yield).[14] Oxymercuration-demercuration of **10** produced the tertiary alcohol **12**, mp 216-218 °C,[15] which was converted to the triacetate **13**, mp 199-201 °C, by Oppenauer's method.[16] Selenium dioxide in dioxane achieved a clean hydroxylation of **13** to yield the hydroxy enone (**14**) mp 196-197.5 °C: NMR δ 5.86, d, J = 2.5 Hz, 7-H. Dehydration to the 7,14-diene-6-one (**15**) (NMR δ 6.18, d, J = 2.5 Hz, 7-H; 5.84, d, J = 2.5 Hz, 15-H; uv (MeOH) 271 nm, ϵ 10 300) occurred readily when a dry pyridine solution of crude **14** was treated with trifluoroacetic anhydride at low temperature;[17,18] the hypsochromic uv shift of ca. 25 nm in **15** as compared to standard 7,14-dien-6-one values shows that the dienone chromophore is distorted, presumably by the fused tetrahydrofuran ring.

Cleavage of the C-16-O bond was accomplished when a pure sample of **15** was treated with excess zinc powder in vigorously stirred boiling acetic acid in the absence of oxygen to yield the desired 8(14),15-diene-6-one, (**16**) (NMR δ 6.32 (16-H) and 6.05 (17-H), ABq, J = 6 Hz; 3.30 and 2.90, ABq, J = 16 Hz, 7-H) a product of concomitant acetyl migration from 25-OH to 22-OH.[19] The crude product **16** was cleanly hydrogenated to the 6,8(14)-enone (**17**), (NMR δ 3.10 and 2.85, ABq, J = 16 Hz, 7-H) which was photooxygenated[20] to the hydroperoxy enone system (**18**) (NMR δ 5.90, d, J = 2 Hz, 7-H; 0.72, s, 18-H; 0.90, s, 21-H). Sodium iodide reduction afforded 5-epi-α-ecdysone 2,3,22-triacetate (**19**), mp 225 °C: NMR δ 5.89, d, J = 2 Hz, 7-H; 0.66, s, 18-H; 0.94, s, 21-H. α-Ecdysone (**1**), mp 170 °C (hydrate), was obtained after basic hydrolysis-epimerization[4b] in a total yield of 1% from diosgenin.[21]

We believe that the procedure described is adaptable to a number of interesting ecdysone analogues, some of which are now being bioassayed for ecdysone or antiecdysone activity, and to the large scale synthesis of α-ecdysone. Furthermore, the scheme allows an easy preparation of [15,16-$^3H_2$]-α-ecdysone, which should be valuable for metabolic studies of insect moulting hormones since the labels are located on unreactive nuclear positions. An alternative route via a 26,27-bisnor-25-methoxycarbonyl side chain which will afford [15,16-$^3H_2$, 26,27-$^{14}C_2$]-α-ecdysone has been completed with cold materials.[22]

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Visible Light to Electrical Energy Conversion. Stable Cadmium Sulfide and Cadmium Selenide Photoelectrodes in Aqueous Electrolytes

Sir:

We wish to report the first sustained conversion of low energy visible light (>1.7 eV) to electrical energy using wet photoelectrochemical cells where there are no net chemical changes in the system.

Irradiation of an n-type semiconductor electrode in a cell as depicted in Scheme I can result in a photocurrent.[1] Use of n-type CdS[2] or CdSe[3] results in photoanodic dissolution to yield Cd^{2+} ions and elemental S or Se. Such a result is typical for semiconductor photoelectrodes with the exception of TiO_2,[4-9] SnO_2,[10] $SrTiO_3$,[11] and $KTaO_3$.[12] Unfortunately, these oxides all have large band gaps (≥3.0 eV) and, consequently, do not respond to visible light. Both CdS (band gap 2.4 eV)[2] and CdSe (band gap ~1.7 eV)[2] respond to a major fraction of the visible spectrum, but the irreversible decomposition encountered in their use as photoelectrodes is a serious hurdle in practice.

An approach to "stabilization" of photoelectrodes is to employ an electrochemically active electrolyte such that its redox chemistry occurs at the expense of electrode decomposition. This approach has proven to yield mixed results. Oxidation of I^- occurs at an irradiated CdS anode, but the

Scheme I

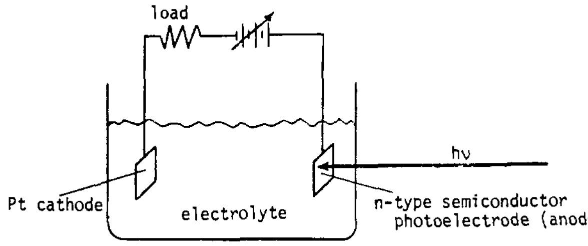

Table I. Photoelectrode Stability and Optical to Electrical Energy Conversion

Crystal[a]	Electrolyte[b]	Crystal before	Crystal after (mol × 10^4)	Electrons generated	Irradiation time, h	V applied	Average i, mA	Power Output, mW	Irradiation λ, nm
CdS-1[c]	1	8.56	8.53	7.73	6.4	+0.25–0.50	3.2		>420[d]
CdS-1[c]	1			25.67	60.5	+0.2–0.40	1.1		>420[d]
	2	5.53	5.44	8.16	24.0	+1.0	0.91		>420[d]
CdS-2	3	8.64	8.64	1.95	11.7	−0.30	0.45	0.14	488[e]
CdSe-1	1	8.78	8.75	23.87	15.35	2.0	4.2		>420[d]
CdSe-1	3	8.43	>7.49[f]	7.76	68.5	−0.15	0.30	0.045	>500[g]
CdSe-1	3			0.32	18.2	−0.15	0.047	0.007	633[h]
CdSe-2	3	8.89	8.89	1.90	49.3	−0.05	0.10	0.005	>500[g]

[a] All crystals used for electrodes are 5 × 5 × 1 mm and the 5 × 5 mm irradiated surface was oriented perpendicular to the *c* axis. The crystals used have the following resistivities: CdS-1, 4.2; CdS-2, 7.3; CdSe-1, 14; CdSe-2, ~15 Ω-cm. All crystals were obtained from the Cleveland Crystal Co., and the resistivities cited were measured by Cleveland Crystal Co. using a four point probe technique. [b] (1) 1.25 M NaOH, 0.20 M Na_2S; (2) 1.25 M NaOH, 0.20 M Na_2S, 1.0 M S; (3) 1.0 M NaOH, 1.0 M Na_2S, 1.0 M S. [c] Data from several runs. [d] Full visible output of superpressure Hg 200 W lamp filtered with 18 cm of H_2O and a Corning glass filter to pass >420 nm wavelength light. [e] From Spectra Physics Argon ion laser, Model 164, beam expanded 6×, power input of ~80 mW. [f] Crystal shattered upon demounting and some material was lost for this reason. [g] Full visible output from 650 W tungsten source filtered with 18 cm of H_2O and a Corning glass filter to pass >500 nm wavelength light, power input of <30 mW. [h] Spectra Physics Model 633 He–Ne laser beam expanded 6×, power input was 2.0 mW.

electrode decomposition could not be quenched even by using high concentrations of I^-.[13] Also, $Fe(CN)_6{}^{4-}$ could be oxidized at an irradiated CdSe electrode yielding stability for an unspecified duration.[3] In this communication we report results on another aqueous electrolyte system where it appears that both CdS and CdSe can be used as *stable* photoelectrodes. Importantly, the photooxidation product can be reduced at the dark cathode to complete a cycle where input light results in current flow (through a load), but no net chemical change results in the system. The principles of such a wet photocell have already been elaborated for CdS, but it was cautioned that electrode stability is a key difficulty.[14] Consequently, we doubt the significance of the high power conversion efficiencies recently reported for a CdS-based cell.[15] The preliminary results of our study are outlined below.

Irradiation of the n-type CdS or CdSe electrode in a cell with 1.0 M NaOH electrolyte results in current flow such that the electrons go towards the Pt electrode. The cell in all photoelectrochemical experiments was a glass cylinder 4 cm in diameter and 10 cm high. The photoelectrode and dark electrode were positioned less than 3 cm apart. Consistent with earlier findings,[2,3] the wavelength onset of the current corresponds approximately to the band gap. The photocurrent is accompanied by obvious, rapid decomposition of the semiconductor electrode, and the maintenance of a steady photocurrent is not possible. However, introduction of Na_2S into the electrolyte leads to a stable photocurrent, and one can detect no decomposition of the semiconductor electrode. Oxidation of the *added sulfide* obtains at the irradiated electrode as evidenced by the formation of a yellow color from the initially colorless solutions, and at the Pt cathode H_2 is initially evolved. If elemental sulfur is added to the electrolyte in sufficient amounts, the H_2 evolution at the Pt electrode ceases, and the competing chemistry is presumably the reduction of some polysulfide species. While a complicated equilibrium exists in aqueous solutions of Na_2S and S,[16] the chemistry occurring in the cell could be represented by the two half cell reactions (1 and 2) occurring at the photoelectrode and the dark electrode, respectively.[17] Since the polysulfides are air sensitive, continuously Ar purged electrolytes were typically used, and, consequently, the results reported are for stirred solutions.

$$\text{A (reduced form)} \rightarrow \text{A (oxidized form)} \quad \text{photoelectrode (anode)} \qquad (1)$$

$$\text{A (oxidized form)} \rightarrow \text{A (reduced form)} \quad \text{dark electrode (cathode)} \qquad (2)$$

To confirm that the electrolyte is undergoing no net chemical change we have passed 2 mA of current (the current density was comparable to a typical photocurrent density) at 0.43 V through an electrolyte consisting of 1.0 M Na_2S, 1.0 M S, and 1.0 M NaOH. This dark electrolysis using two Pt electrodes was carried out in a sealed spectroscopic cell (1-mm pathlength) using a 2.0-cm^3 volume of electrolyte under Ar. Only small visible absorption spectral changes were detectable for the solution even after the passage of 2×10^{-3} mol of electrons, and the current was invariant (±2%). If the redox processes were irreversible this would correspond to considerable consumption of the redox active components.

The data in Table I provide quantitative measures of the stability of both CdSe and CdS photoelectrodes in basic electrolytes containing Na_2S. In some cases we observe some decline in photocurrent with prolonged irradiation, but in no case have we ever observed the photocurrent to cease, nor have we ever observed significant weight loss in the crystal. We do see some surface discoloration at the highest light intensities used. It is very likely that at some high light intensity electrode decomposition will not be quenched due to diffusion limiting rates. The role of the *added sulfide* is to apparently quench photoelectrode decomposition by undergoing oxidation at the expense of either the sulfide or selenide of the CdS or CdSe, respectively. It is possible that an exchange of the sort $CdSe + S^{2-} \rightarrow CdS + Se^{2-}$ could occur at the surface of the CdSe, but we have not yet characterized the surface of CdSe after exposure to the $Na_2S|S$ electrolyte. However, there is no obvious CdS formation on the CdSe crystal by visual observation.

Stabilization of the photoelectrode by the added Na_2S is remarkable, but the conversion of optical to electrical energy requires the ability to observe a photocurrent with a load in the external circuit. For CdS and CdSe we have observed the onset of photocurrent to be as negative as −0.8 and −0.45 V, respectively. These values do depend somewhat on light intensity as expected,[2] but the important fact is that sustained, positive optical to electrical energy conversion can be obtained without chemical deterioration of any of the components. Table I summarizes the results for several long term irradiations carried out at negative bias (the power supply is the load). At this writing the maximum optical to electrical energy conversion that we have observed is ~1.2% for CdSe (at −0.2 V) and ~0.9% for CdS (at −0.35 V). The experiment in Table I for CdSe irradiated with a He–Ne laser is typical: the 6× expanded 633 nm beam gave 2.0 mW of uniform irradiation on the 0.25 cm^2 exposed surface of the CdSe. At −0.15 V a photocurrent of 0.047 mA (a quantum yield for electron flow of 0.046) was observed corresponding to a power output of at least 7 × 10^{-3} mW. The power conversion efficiency is then (7 × 10^{-3})/2 or 0.35%. Efficiency has not been optimized, but these experiments establish the importance of chemical stabilization of the photoelectrode. The details of these studies, along with results of attempts to increase efficiency, will be reported subsequently.

Note Added in Proof. We have now found that etching the CdS and CdSe leads to significantly improved efficiencies: ∼5% for CdS at 500 nm and up to ∼9% for CdSe at 633 nm in a 1 M Na_2S, 1 M S, 1 M NaOH aqueous electrolyte. Stability is still maintained at these high power conversion efficiencies.

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Ground and Excited State Correlations in the Rupture of Oxygen–Oxygen Bonds in Peroxides

Sir:

The ground state rupture of peroxide bonds is known to be involved in a number of condensed phase chemi- and bioluminescence reactions.[1] In addition, the photodecomposition of the peroxide linkage is used as a method of generating a number of radical species.[2] There is, however, some question about the photochemical nature of the states reached by photoexcitation. In particular, it is not generally recognized[3] that besides the ground state of hydrogen peroxide a number of singlet and triplet excited states are adiabatically correlated with the two ground state hydroxyl radicals. However, in a recent review article[4] Dauben, Salem, and Turro classified the rupture of a peroxide bond as being of the $(\sigma\pi)(\sigma\pi)$ type showing that a total of four pairs of diradical states are possible. This paper will show that this is computationally correct. We will also propose a simple bonding argument to show why it is correct.

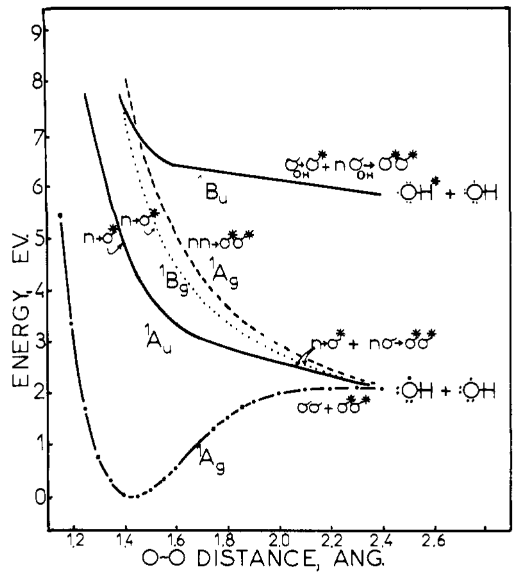

Figure 1. Ground and excited singlet correlations in *trans*-H_2O_2. The n orbital is either n_1 or n_2 (see text), while the σ or σ^* refers to the oxygen bonding and antibonding orbitals. Also shown are the principal configurations at short (1.4 Å) and long distances (2.0 Å).

Shown in Figure 1 is the cross section of a semiempirically computed potential energy surface for the rupture of the O–O bond in trans (C_{2h}) hydrogen peroxide. This computation was achieved using a combination of the Eaker–Hinze[5] and DasGupta–Huzinaga[6] modifications of the CNDO/2 parameterization. The latter modification was used to approximate the experimental bond dissociation energy[7] of H_2O_2 (ca. 2 eV). This modified CNDO technique was used to generate the wave functions necessary for a configuration interaction estimate of the ground and excited single and triplet states. Approximately 80 configurations of the single and double excitation type were used for the singlet surfaces. Detailed analysis of the configurational wave functions showed no unexpected features. In addition, test calculations indicated that triple excitations were not of relative importance for correlating the states in question. Although the calculations were only calibrated to reproduce the approximate O–O bond energy, reasonable estimates were obtained for the excitation energies of peroxides[2] and the hydroxyl radical,[8] the ground state heat of atomization, and the O–O bond distance at the energy minimum.[9] The O–O force constant is too high, but better than previous semiempirical calculations.[9] Although all semiempirical calculations suffer from being parameter dependent, the imposition of configuration interaction at a modest level assures that the curves shown have utility as semiquantitative state correlation diagrams, provided that Rydberg type transitions are not important.

The unusual nature of the singlet surfaces shown in Figure 1 is that a total of four molecular states, 2 ^1A_g, ^1A_u, and ^1B_g, correlate with two ground state hydroxyl radicals. Corresponding calculations also showed four triplet states, all