# A Double Photoelectrode-Based Cell for the Conversion of Light to Electricity: p-Type CdTe and n-Type CdSe Photoelectrodes in a Polysulfide Electrolyte

*Sir:*

Considerable success has been realized recently[1-9] in converting visible light to electricity using n-type semiconductor-based photoelectrochemical cells. Success[1-7] with nonoxide semiconductor photoelectrodes has hinged on the ability to (1) quench the photoanodic decomposition of the photoelectrode, and (2) find electrolytes which undergo no net chemical change upon irradiation and passage of current. In principle, p-type semiconductors should be useful as photocathodes in an electrochemical cell, and, importantly, some p-type semiconductors studied to date do seem to be stable when used as photocathodes.[10-12] However, the reduction of substances other than $H_2O$ has not been demonstrated. We now report that p-type CdTe can be used as a photocathode for the reduction of polysulfides, $S_n^{2-}$, and can be used in a photoelectrochemical cell for the conversion of light to electricity. Further, we outline preliminary results on the first double photoelectrode-based cell employing an electrolyte which undergoes no net chemical change.

Visible light irradiation of a p-type, single-crystal CdTe (band gap, $E_{BG} = 1.4$ eV)[13] electrode in 1 M NaOH results in a photocathodic current with $H_2$ evolution at potentials slightly more positive (50–100 mV) than thermodynamically expected. Little or no cathodic current flows in the dark. Similar results obtain if the electrolyte is 1.0 M NaOH, 1.0 M $Na_2S$ where $H_2O$ is the electroactive substance at the photocathode. The noteworthy result is that, if the electrolyte is 1.0 M NaOH, 1.0 M $Na_2S$, 1.0 M S evolution of $H_2$ is not observed, and the electroactive substance at the photocathode is apparently the $S_n^{2-}$ which is reducible in competition with the $H_2O$. In the $S_n^{2-}$ electrolyte the onset of photocathodic current is about 150 mV more positive than thermodynamically expected (−0.7 V vs. SCE is the redox potential of $S^{2-}/S_n^{2-}$).[14]

To verify that $S_n^{2-}$ is reduced at the photocathode and oxidized at the counterelectrode we determined that the electrolyte composition in a miniphotoelectrochemical cell is constant with prolonged photoelectrochemical action. The cell, 20 × 20 × 2 mm, containing 0.24 mL of the Ar-purged $S_n^{2-}$ electrolyte, consisted of a p-type CdTe photocathode, a Pt anode, and a $Ag_2S$ reference electrode. The $Ag_2S$ reference was prepared in situ by oxidizing a Ag wire vs. the Pt electrode. Epoxy was used to seal the cell under Ar. Irradiation of the p-type CdTe (potentiostatted at −0.20 V vs. $Ag_2S$ which

Scheme I

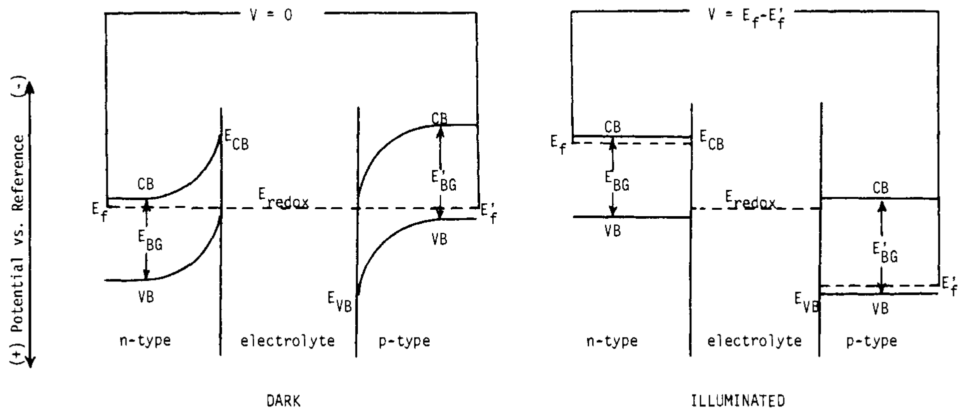

**Table I.** Stability of Photoelectrodes in Aqueous $S_n^{2-}$ Electrolytes[a]

| Electrode system, cathode vs. anode | Moles × $10^4$ [b] Before | After | Electrons | Photocurrent, mA | Open-circuit photopotential, mV[c] |
|---|---|---|---|---|---|
| p-CdTe (**1**) vs. Pt | 3.39 | 3.36 | 5.38 | 0.74 | |
| | 3.43 | 3.35 | 9.36 | 1.40 | 150 |
| | 2.48 | 2.39 | 8.46 | 0.47 | |
| p-CdTe (**2**) vs. Pt | | | | | 100 |
| n-CdSe vs. Pt | | | | | 500 |
| p-CdTe (**2**) vs. n-CdSe | 2.40<br>4.84 | 2.38<br>4.73 | 4.65 | 0.52 | 580 |
| p-CdTe (**1**) vs. n-CdSe | 1.42<br>6.88 | 1.41<br>6.83 | 5.02 | 0.49 | |

[a] The electrolyte is an Ar-purged 1.0 M NaOH, 1.0 M $Na_2S$, 1.0 M S solution at 298 K. Irradiation is with the full visible (UV and IR filtered) output from one (two) Bausch and Lomb 200-W Hg lamp(s) focused onto the photoelectrode(s). The single crystal p-type CdTe and n-CdSe were from Cleveland Crystals, Inc. The p-CdTe was either ~1500 Ω cm (p-CdTe (**1**)) or ~3800 Ω cm (p-CdTe (**2**)) and the exposed surface was ~5 × 5 mm. The n-CdSe is the same as used previously.[1,3] The electrodes were prepared as described previously[1-5] except the contact to p-CdTe was made with electroless Au plating. In experiments where p-CdTe was irradiated in a cell with a Pt anode the CdTe was potentiostatted at −1.00 or −1.05 V vs. SCE. In the experiments with a p-CdTe photocathode and an n-CdSe photoanode the two electrodes were irradiated either at short circuit or in series with a power supply such that the p-CdTe potential was at −1.00 ± 0.05 V vs. SCE during the experiment. [b] Comparison of electrode composition (determined by weight) before and after the passage of the indicated current. The small weight losses found are associated with demounting the single crystal.[1-3] [c] Potential difference between anode and cathode upon irradiation under typical irradiation conditions used here. Upon irradiation p-CdTe potential moves more positive and the n-CdSe moves more negative relative to the Pt electrode which is at the $S^{2-}/S_n^{2-}$ potential of −0.7 V vs. SCE; 150 mV is the highest photopotential of p-CdTe vs. Pt but the n-CdSe vs. Pt has been observed to be up to 700 mV.[3]

corresponds to −1.05 V vs. SCE) with the full visible output of a 200-W Hg lamp yielded a stable ~2.4 mA/cm$^2$ photocurrent. During an irradiation period where enough electrons were passed to consume >150% of the electroactive $S_n{}^{2-}$ we found that the $Ag_2S$ vs. Pt potential changed only slightly from −0.126 to −0.132 V. Moreover, optical density of the $S_n{}^{2-}$ electrolyte changed from only 0.455 to 0.480 at 501.7 nm and 0.579 to 0.591 at 496.5 nm. Significantly, no $H_2$ evolution was observed. The small changes that are observed are likely due to a redistribution of the $S_n{}^{2-}$ species, an effect previously observed.[3]

Photoelectrode stability is evidenced by (1) constant photocurrents, (2) no obvious change in the electrode surface, and (3) constant weight of the CdTe before and after significant photoelectrochemical action, Table I. Thus, the electrode and electrolyte are stable for the p-type CdTe-based photoelectrochemical cell employing the $S_n{}^{2-}$ electrolyte. The p-type CdTe-based cell, however, inefficiently converts light to electricity, since the open-circuit photopotential has been found to be only ~150 mV and short-circuit quantum yields for electron flow are of the order of only 0.002. These low values may be due, in part, to the low carrier concentration (~10$^{14}$ cm$^{-3}$) in the p-type CdTe.

The results above afforded us the opportunity of demonstrating the first double photoelectrode-based cell for the conversion of light to electricity, since it had been previously demonstrated that CdSe ($E_{\mathrm{BG}}$ = 1.7 eV) is a stable photoanode in the $S_n{}^{2-}$ electrolyte.[1,3] For the conversion of light to electricity, a key advantage in a double photoelectrode cell is that the maximum output voltage, $V$, can be higher. The ideal energetic situation is as sketched in Scheme I where the valence band position, $E_{\mathrm{VB}}$, for the n-type material is just below the electrolyte redox level, $E_{\mathrm{redox}}$, and the conduction band position, $E_{\mathrm{CB}}$, for the p-type material is just above $E_{\mathrm{redox}}$.[12] For fairly high carrier concentration the Fermi level in the n-type material, $E_{\mathrm{f}}$, is close to $E_{\mathrm{CB}}$, and in the p-type material the Fermi level, $E_{\mathrm{f}}'$, is close to $E_{\mathrm{VB}}$. Consequently, the value of $V$ upon illumination, $E_{\mathrm{f}} - E_{\mathrm{f}}'$, can approach the sum of the band gaps of the two materials $E_{\mathrm{BG}} + E_{\mathrm{BG}}'$.

The n-type CdSe-, p-type CdTe-based cell is far from ideal but is illustrative. First, irradiation of the CdSe and CdTe does yield a stable photocurrent with neither change in the electrolyte or the electrodes, Table I. The maximum open-circuit potential difference between CdSe and CdTe upon simultaneous irradiation is larger than for either CdSe or CdTe against a Pt electrode. However, the total energy conversion efficiency of the cell is less than for CdSe alone, since the p-type CdTe provides relatively little driving force (maximum of 150 mV) and yet it still must be irradiated in order for any current to flow. Qualitatively, the CdSe/CdTe based cell is at most a little over one-half as efficient as the n-type CdSe-based cell alone, since twice as many photons are required to raise the maximum output potential from ~700 mV for CdSe[1,3] alone to ~850 mV for the double photoelectrode-based cell. A mismatch in the photocurrent efficiencies in p-type CdTe and n-type CdSe contributes further to inefficiency.[15]

Though the p-type CdTe-based cell efficiency is disappointing, we are encouraged by the fact that we have demonstrated that substances other than $H_2O$ can be reduced with 100% efficiency at p-type photocathodes. Preliminary results with other p-type materials (p-GaAs, GaP) in polychalcogenide electrolytes show similar behavior and these will be discussed in the full paper.[19]

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## References and Notes

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(14) This energetic development follows from the principles previously outlined: H. Gerischer, *J. Electroanal. Chem.*, **58**, 263 (1975), and references therein.
(15) The optimum efficiency of the double photoelectrode-based cell depends on a number of factors including the relative intensity at the two photoreceptors. These features will be elaborated in the full paper.
(16) Fannie and John Hertz Fellow.
(17) Work performed while a Visiting Scientist at M.I.T. on sabbatical leave from the Department of Chemistry, California State University, Long Beach, Calif.
(18) Recipient of a Dreyfus Teacher-Scholar Grant, 1975–1980.
(19) Note Added in Proof. Aside from the related work in ref 10–12, a number of related reports on p-type photoelectrodes have recently appeared: (a) H. Tributsch, *Ber. Bunsenges. Phys. Chem.*, **81**, 361 (1977); (b) A. J. Nozik, *Appl. Phys. Lett.*, **30**, 567 (1977); **29**, 150 (1976); (c) M. Tomkiewicz and J. M. Woodall, *Science*, **196**, 990 (1977); and (d) K. Ohashi, J. McCann, and J. O'M. Bockris, *Nature (London)*, **266**, 610 (1977).

**Jeffrey M. Bolts, Arthur B. Ellis,[16] Kenneth D. Legg[17]**
**Mark S. Wrighton*[18]**
*Department of Chemistry*
*Massachusetts Institute of Technology*
*Cambridge, Massachusetts 02139*

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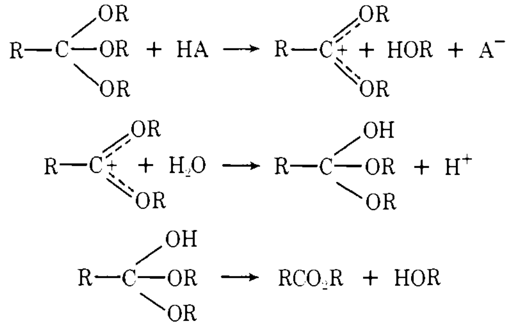
## Ortho Ester Hydrolysis. The Complete Reaction Mechanism

*Sir:*

The mechanism for the acid-catalyzed hydrolysis of ortho esters is generally believed to consist of three separate reaction stages:[1] (1) generation of a dialkoxy carbonium ion, (2) hydration of this ion to a hydrogen ortho ester, and (3) breakdown of the latter to alcohol and carboxylic acid ester products (eq 1-3).



$$\mathrm{R{-}C(OR)_3} + \mathrm{HA} \longrightarrow \mathrm{R{-}\overset{+}{C}(OR)_2} + \mathrm{HOR} + \mathrm{A^-} \tag{1}$$

$$\mathrm{R{-}\overset{+}{C}(OR)_2} + \mathrm{H_2O} \longrightarrow \mathrm{R{-}C(OH)(OR)_2} + \mathrm{H^+} \tag{2}$$

$$\mathrm{R{-}C(OH)(OR)_2} \longrightarrow \mathrm{RCO_2R} + \mathrm{HOR} \tag{3}$$

Although this is a reasonable reaction mechanism, the process has invariably been studied only under conditions where the first stage is rate determining and there is therefore no direct kinetic evidence for the rest of the reaction scheme. We wish to report that we have now found conditions under which stage 3 is rate determining and that we have also observed the interconversion of the reactants and products of