Interaction of Thiols with n-Type Cadmium Sulfide and n-Type Cadmium Selenide in Aqueous Solutions: Adsorption of Thiolate Anion and Efficient Photoelectrochemical **Oxidation to Disulfides**

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Organic thiols, RSH = cysteamine, 2-mercaptoethanol, penicillamine, or cysteine, effectively suppress photoanodic decomposition of n-CdS and n-CdSe in aqueous solutions and undergo efficient controlled potential photoelectrochemical oxidation to the corresponding disulfides, RSSR. Photovoltage (the extent to which oxidation occurs at potentials negative of the thermodynamic potential) of greater than 700 mV is observed for certain thiols upon excitation of the semiconductor anode with light of energy greater than the band gap. As electrodes for preparative electrosynthesis, both illuminated n-CdS and n-CdSe offer significant electrical energy savings compared to conventional electrochemical oxidation in the dark at a Pt electrode. The oxidation of RSH to RSSR at n-CdS and n-CdSe has been studied under various conditions: high current efficiencies, typically measured to be greater than 98%, are found at high and low pH for all RSH studied except glutathione which is oxidized with about 60% current efficiency. Attempted controlled potential oxidation of glutathione at n-CdS leads to decomposition of the electrode. No S/Se exchange occurs at the surface of n-CdSe in the efficient photoelectrochemical oxidation of RSH to RSSR, as determined by Auger spectroscopy. The output parameters at n-CdS and n-CdSe depend on the nature of the functional groups on the RSH. The best energy conversion performance is achieved with a 1 M solution of cysteamine at pH 11 with an efficiency for conversion of 501.7-nm light (30 mW/cm²) to electricity of 14.5% (without electrode decomposition) with a photovoltage of 670 mV when n-CdS is used as a photoanode. In contrast, a 1 M glutathione solution at pH 11 yields an efficiency of only 0.6% (with electrode decomposition) with a photovoltage of 510 mV under the same conditions. Both capacitance-voltage and photocurrent-voltage measurements show that the flat-band potentials, E_{FB} , of n-CdS and n-CdSe are shifted to more negative values (by up to 0.7 V) by the strong adsorption of RS⁻. Unfortunately, a simple Langmuir model does not explain the concentration dependence of adsorption of RS⁻ and detailed comparisons of binding properties cannot be made.

We wish to report some new results relating to specific interaction of redox substrates, organic thiols (RSH), with semiconductor photoelectrodes, n-CdS and n-CdSe, that leads to highefficiency photoelectrochemical oxidation processes which compete effectively with photoanodic decomposition of the semiconductors. Part of the significance of the results rests in the fact that the strong adsorption of RSH onto CdX (X = S, Se) makes these electrodes superior electrodes for the purpose of oxidation of RSH to form RSSR. It is likely that the development of useful applications of photoelectrochemical synthesis will involve cases where the redox chemistry can be done uniquely well at the semiconductor electrode. Accordingly, exploration of the specific interactions of redox substrates with semiconductor surfaces is now under investigation in this laboratory. A recent paper describes studies of the interaction of dithiocarbamates with n-CdS and n-CdSe in nonaqueous electrolyte solutions.¹ As for the dithiocarbamates, study of thiols is likely to be quite fruitful, since there are a large number of variations possible, in terms of electronic and geometric structure. Some earlier work on organic thiols has been reported,^{2,3} but this article represents the first investigation of the behavior of organic thiols at single-crystal n-CdS and n-CdSe.

Strongly interacting redox substrates have proven crucial to the development of efficient photoelectrochemical devices for the conversion of light to electricity.^{4,5} In fact, the first significant





stabilization of small band gap, $E_{\rm g}$, (visible light-responsive) n-type semiconductors to photoanodic decomposition involved the use of aqueous polychalcogenide redox systems, X_n^{2-} (X = S, Se, Te) to suppress decomposition of n-CdX (X = S, Se, Te) electrodes.⁴ The ruggedness of n-CdS in the presence of strongly interacting S_n^{2-} , for example, is a consequence of the ability of the S_n^{2-} to effectively scavenge the photogenerated oxidizing equivalents, h⁺, that become available at the top of the valence band in contact

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⁽¹⁾ Thackeray, J. W.; Natan, M. J.; Ng, P.; Wrighton, M. S. J. Am. Chem. Soc. 1986, 108, 3570.

^{(2) (}a) Dewitt, R.; Kirsch-De Mesmaeker, A. J. Electrochem. Soc. 1983, 130, 1995. (b) Josseaux, P.; Kirsch-De Mesmacker, A.; Riga, J.; Verbist, J. J. Electrochem. Soc. 1983, 130, 1067. (c) Dewitt, R.; Kirsch-De Mesmacker, A. Appl. Phys. Lett. 1984, 45, 146. (d) Josseaux, P.; Kirsch-De Mesmaeker, A.; Roche, A.; Romand, M.; Montes, H. J. Electrochem. Soc. 1985, 132, 684. (e) Kirsch-De Mesmacker, A.; Josseaux, P.; Nasielski, J.; Defosse, C. Sol. Energy Mater. 1982, 6, 429. (f) Kirsch-De Mesmacker, A.; Decoster, A. M.; Nasielski, J. Sol. Energy Mater. 1981, 4, 203.

⁽³⁾ Aruchamy, A.; Venkatarathnam, A. Subrahamnyam, M.; Subba Rao,

<sup>G. V.; Aravamudan, G. Electrochim. Acta 1982, 701.
(4) (a) Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. J. Am. Chem. Soc.
1976, 98, 1635. (b) Hodes, G.; Manassen, J.; Cahen, D. Nature (London)</sup> 1976, 261, 403. (c) Miller, B.; Heller, A., Nature (London) 1976, 262, 680.

^{(5) (}a) Tributsch, H. J. Electrochem. Soc. 1978, 125, 1086. (b) Gobrecht, (a) Inolusci, H. J. Electrochem. Soc. 1978, 125, 1060. (b) Gobelent,
 J.; Tributsch, H.; Gerischer, H. J. Electrochem. Soc. 1978, 125, 2085. (c)
 Kline, G.; Kam, K.; canfield, D.; Parkinson, B. A. Sol. Energy Mater. 1981,
 4, 301. (d) Kline, G.; Kam, K.; Canfield, D.; Parkinson, B. A. Sol. Energy Mater. 1982, 6, 337. (e) Heller, A.; Parkinson, B. A.; Miller, B. Appl. Phys.
 Lett. 1978, 33, 521. (f) Heller, A.; Lewerenz, H. J.; Miller, B. Ber. Bunsenges.
 Phys. Chem. 1980, 84, 592. (g) Calabrese, G. S.; Wrighton, M. S. J. Am. Chem. Soc. 1981, 103, 6273.

with the electrolyte solution, E_{VB} , Scheme I. The h⁺ oxidizes the redox substrate at a net efficiency that precludes photoanodic decomposition according to eq 1. Subsequently, there have been

$$CdS (or CdSe) + 2h^+ \rightarrow Cd^{2+} + S (or Se)$$
(1)

many demonstrations of the use of redox reagents, in solution and bound to the surface of the semiconductor, to substantially suppress the photoanodic decomposition of n-type semiconductors.⁶

The ability to completely suppress the photoanodic decomposition of small E_{g} semiconductors allows the claim that one can sustain the conversion of visible light, including solar energy, to electricity (or chemical energy) with high efficiency and for long periods of time. When the electrochemical potential of the semiconductor, $E_{\rm f}$, can be held at a potential more negative than the electrochemical potential of the solution, E_{redox} , and there is photocurrent,4-6 as shown in Scheme I, there is positive efficiency for the conversion of optical energy. The maximum extent to which the photocurrent, *i*, onsets at an electrode potential, E_{f} , that is more negative than $E_{\rm redox}$ is the open-circuit photovoltage, $E_{\rm V(oc)}$, and the extent to which $E_{\rm f}$ is more negative than $E_{\rm redox}$ when the photocurrent is the photovoltage, E_V , Scheme I. The onset of photocurent generally corresponds closely to the so-called flat-band potential, $E_{\rm FB}$, the value of $E_{\rm f}$ where there is no band bending. The $E_{\rm FB}$ can also be determined by measuring the interface capacitance as a function of $E_{\rm f}$.⁷ The objective in energy conversion is to maximize the product of photocurrent and photovoltage at a given incident optical power, in order to achieve the highest power conversion efficiency, eq 2.

$$\eta_{\rm max} = \left[(E_{\rm V}i)_{\rm max} / \text{optical power} \right] \times 100\%$$
(2)

The interaction of several thiols with polycrystalline n-CdS has been examined.² Photocurrent-voltage curves and interfacial capacitance studies show that the thiols interact strongly and in favorable ways with the CdS. In this work, we demonstrate that organic thiols stabilize single-crystal n-CdX (X = S, Se) to photoanodic dissolution, and that efficient photoelectrochemical oxidation to the disulfide, eq 3, takes place not only with high

$$2RSH + 2h^+ \rightarrow RSSR + 2H^+$$
(3)

current efficiency but with a high energy conversion efficiency, with appropriate choice of R- group. In this work with the polycrystalline CdS long-term durability was not achieved,² possibly because the electrode potential was held at more positive values than required to effect the photoelectrochemical oxidation. Additionally, the differences in chemical composition and structure of the polycrystalline vs. single crystal surfaces can affect the durability. Our work has shown that long-term durability is possible when the electrode is held close to the so-called maximum power point on the photocurrent-voltage curve. In addition, photocurrent onset and capacitance measurements reveal that adsorption of thiolate, the deprotonated thiol, is solely responsible for shifts of E_{FB} of single-crystal n-CdS and n-CdSe in aqueous solutions of RSH/RS⁻. In the polycrystalline samples of CdS a pH-dependent shift of $E_{\rm FB}$ was found that we do not find for the single-crystal surfaces investigated here; the difference may lie in the presence of an oxide on the surface of the polycrystalline CdS.2

Experimental Section

Electrode Preparation. Single crystals of low-resistivity (1-5 ohm-cm) n-CdS and n-CdSe, cut perpendicular to the c axis, were obtained from Cleveland Crystals, Inc. The crystals were approximately 1-mm thick and were cut into small pieces with a diamond-blade string saw. The CdS crystals were etched in concentrated HCl for 30 s and rinsed with a large volume of H_2O . The CdSe crystals were etched in aqua regia, rinsed with distilled H_2O_1 , and then soaked for 5 min in a concentrated aqueous solution of KCN, before a final rinse with a large volume of distilled H_2O . Most experiments were carried out using the shiny Cd-rich faces of the polar (0001) crystals of n-CdS and n-CdSe.⁸ The donor densities, determined from the slopes of Mott-Schottky plots, were typically 1×10^{17} cm⁻³ for both materials.

Reagents. Penicillamine, 2-mercaptoethanol, 3-mercaptopropionic acid (and its methyl ester), 3,3'-dithiodipropionic acid, 2-hydroxyethyl disulfide, and penicillamine disulfide were purchased from Aldrich Chemical Co. and used as received. Reduced and oxidized glutathione, cysteine, cystine, 2-mercaptoethylamine (cysteamine), 2-mercaptoethanesulfonic acid, cysteine ethyl ester, and cystamine were used as received from Sigma Chemical Co. Several of the thiols listed above were also obtained from Fluka Chemical Co. Aqueous solutions were prepared by dissolving appropriate reagents in triply distilled H₂O (18 Mohm) or MCB Omnisolv HPLC grade H₂O. Na₂SO₄ electrolyte was used as obtained from Mallinckrodt. MCB Omnisolv H₂O and MeOH were used as solvents for the HPLC.

Equipment. Current-voltage data were obtained by using a Princeton Applied Research (PAR) Model 173 or ECO Model 551 potentiostat driven with a PAR Model 175 universal programmer. For all experiments, a calibrated saturated calomel electrode (SCE) was the reference electrode and a clean Pt foil of area 3 cm² was the counter electrode. Current-voltage data were plotted with a Houston Instruments Model 2000 X-Y recorder. The current vs. time plots were recorded with a Hewlett-Packard 7133A or Varian A-44 strip chart with an ESC digital coulometer. Current-voltage curves were recorded at 2 or 5 mV/s, using stirred, N₂- or Ar-purged solutions. Controlled potential oxidations were performed in two-compartment cells separated by a medium or fine glass frit.

Capacitance measurements were made with a PAR Model 5204 lock-in analyzer to generate an ac signal of amplitude 4-7 mV peak-to-peak, at frequencies between 500 Hz and 10 kHz. Calibration was made using an externally constructed RC circuit, whose linearity was established prior to each measurement. All measurements were taken in complete darkness in a quiet solution, at a rate of 2 mV/s. The data were analyzed by using a Hewlett-Parckard 85 computer and plotted with the Hewlett-Packard 1140 plotter.

The light sources for illumination of n-CdS were a focused 200-W tungsten-halogen lamp or a beam-expanded Spectra Physics Model 164 laser at 501.7 nm; for illumination of n-CdSe an Aerotech beam-expanded He-Ne laser at 632.8 nm was used. Light intensities were measured with a Tektronix J16 radiometer equipped with a J6502 probe, and a calibrated Solarex Corp. photometer. The intensities were varied by using a Variac variable voltage source or a photographic polarizing filter. The areas of illumination were adjusted by using precision diameter masks.

High-Pressure Liquid Chromatography. Current efficiencies were monitored by using the Hewlett-Packard 1084B HPLC equipped with a Hewlett-Packard 1040 Rapid-scan UV-vis detector, or with a Waters Associates 6000A HPLC. Detection was made at 254 nm, and separations were accomplished with an Alltex C_{18} reversed phase 5-µm column (250 mm × 4.6 mm i.d.) or an H-P C₈ RP-8 5- μ m column (200 mm × 4.6 mm i.d.) with MeOH/H₂O solvent mixtures buffered with 0.008% to 0.2% v/vtrifluoroacetic acid, depending on the particular thiol/disulfide couple to be separated. Identities of molecules associated with the peaks were established by comparison of rapid scan UV-vis spectra and retention times with injected authentic samples of the thiols and disulfides in the same electrolyte. Linear plots of integrated peak area vs. concentration of authentic samples were

^{(6) (}a) Horowitz, G.; Tourillon, G.; Garnier, F. J. Electrochem. Soc. 1984, 131, 151. (b) Noufi, R.; Frank, A. J.; Nozik, J. J. Am. Chem. Soc. 1981, 103, 1849. (c) Fan, F. F.; Wheeler, B. L.; Bard, A. J. J. Electrochem. Soc. 1981, 128, 2042. (d) Skotheim, T.; Lundstrom, I.; Prezja, J. J. Electrochem. Soc. 1981, 128, 1625. (e) Skotheim, T.; Petersson, G. L.; Inganas, O.; Lundstrom, I. J. Electrochem. Soc. 1982, 129, 1737. (f) Rubin, H. D.; Humphrey, B. D.;
 Bocarsly, A. B. Nature (London) 1984, 308, 339. (g) Rosenblum, M. D.;
 Lewis, N. S. J. Phys. Chem. 1984, 88, 3103.
 (7) Myamlin, V. A.; Pleskov, Y. V. Electrochemistry of Semiconductors;

Plenum: New York, 1967.

⁽⁸⁾ Warekois, E. P.; Lavine, M. C.; Mariano, A. N.; Gatos, H. C. J. Appl. Phys. 1962, 33, 690.



Figure 1. Steady-state photocurrent-voltage curves (5 mV/s) for n-CdS in 0.1 M 2-mercaptoethanol/0.1 M Na2SO4 at pH 7.2, initially and after 24 h of irradiation. The inset shows the current density obtained over the 24-h period. The excitation source was a tungsten-halogen lamp.

found and integrations were thus used to quantitatively measure disulfide concentration in the anolyte compartment of photoelectrochemical cells.

Auger and X-ray Photoelectron Spectroscopy and Electron Microscopy. Auger spectra were obtained with a Physical Electronics Model 590A scanning Auger spectrometer. A 5-keV electron beam with a beam current of $0.1-1 \ \mu A$ was used as the excitation source. A Physical Electronics Model 04-303 differential ion gun was used to produce a 2-keV Ar⁺ ion beam for sputtering. X-ray photoelectron spectra were obtained on a Physical Electronics Model 548 spectrometer with a magnesium anode. The broad scans were recorded with a pass energy of 100 eV and the narrow scans with a pass energy of 25 eV. Elements detected by Auger and XPS were identified by reference to data previously reported, obtained by using these techniques.⁹ The SEM photographs were obtained by using a Cambridge Mark 2A stereo scanning electron microscope with resolution of 20 nm.

Results and Discussion

Study of the behavior of n-CdX (X = S, Se) photoanodes in aqueous solution containing one of a variety of organic thiols, RSH, shows the general result that sustained oxidation of RSH can be effected in a thermodynamically uphill sense to quantitatively form RSSR. The same essential result is obtained for all RSH, except for glutathione which is unsuccessful in completely suppressing decomposition of the illuminated n-CdX. However, the efficiency of the conversion of optical energy depends significantly on the nature of the R- group. Additionally, there are important consequences associated with variation in pH that relate to the shift in $E_{\rm FB}$ of the n-CdX as a consequence of RS⁻ adsorption. In the sections below we detail the experiments that establish the photoelectrochemical behavior of the n-CdX/RSSR/RSH/RS⁻ system in aqueous solution.

Controlled Potential Electrolyses. Figure 1 shows the steady-state photoelectrochemical behavior of n-CdS, at pH 7.2, in the absence and presence of 0.1 M 2-mercaptoethanol. The addition of RSH is associated with a large increase in anodic current, ostensibly due to oxidation of RSH. The photocurrent-voltage curve in the presence of the RSH shows a slight improvement (more negative onset) after a short period of steady-state photoelectrochemical oxidation. The changes in the photocurrent-voltage curve can be attributed to a photoetching of the surface in the initial period of photoelectrolysis that does not correspond to a significant amount of charge passed.¹⁰ Controlled potential (-0.5 V vs. SCE) photoelectrochemical oxidation of 2-mercaptoethanol in a two-compartment cell can be



Figure 2. HPLC chromatograms vs. charge passed during a controlled potential photoelectrolysis of 1.0 M 2-mercaptoethanol/0.1 M Na₂SO₄/pH 10.5 solution using a CdSe photoanode exited by a tungsten-halogen lamp. HPLC conditions: 12% MeOH/H2O/0.2% CF3-COOH, 1.0 mL/min, reverse phase C8 column. (a) Initial chromatogram at 0 C passed. The inset shows the rapid-scan UV-vis spectrum of the peak eluted (2-mercaptoethanol). (b) Final chromatogram at 200 C passed. The insets show the rapid-scan UV-vis spectra of peaks eluted (2-mercaptoethanol followed by 2-hydroxyethyl disulfide). Data in this figure correspond to entry 8 in Table I.

sustained at illuminated n-CdS, as demonstrated by the nearly constant photocurrent of 20 mA/cm² for 24 h, Figure 1.

Analysis of the anolyte of the two-compartment photoelectrochemical cell was performed periodically by HPLC. The chromatograms show gradual disappearance of a peak due to the starting material with concomitant growth of a peak corresponding to 2-hydroxyethyl disulfide. Figure 2 shows representative data for the various systems studied. The identities of the substances associated with the chromatographic peaks were confirmed by comparison (retention time and UV-vis spectrum) to injected authentic samples. The HPLC analyses allow the conclusion that the current efficiency for RSSR formation, defined as the percentage of integrated current attributable to disulfide formation, is within experimental error 100%. Thus, quantitative photoelectrochemical oxidation of 2-mercaptoethanol to 2-hydroxyethyl disulfide, eq 4, occurs at illuminated n-CdS. Apparently, all

$$2h^+ + 2HOCH_2CH_2SH \rightarrow$$

HOCH₂CH₂S-SCH₂CH₂OH + 2H⁺ (4)

photogenerated h⁺'s reaching the surface of the electrode yield oxidation of the RSH to RSSR, not oxidation of the semiconductor.

The oxidation process represented by eq 4 can be effected at a clean Pt electrode, Figure 1. However, the steady-state current-voltage curve worsens with time in the sense that more positive potentials are required in order to maintain a given current density. The deterioration of the performance of the Pt electrode is likely due to fouling of the electrode. By applying a potential of +1.2 V vs. SCE to the Pt electrode, high current efficiency

^{(9) (}a) Davis, L. E.; MacDonald, N. C.; Palmberg, P. W.; Riach, G. E.; Weber, G. E. Handbook of Auger Electron Spectroscopy, 2nd ed.; Perkin-Elmer Corp.: Eden Prairie, MN, 1976. (b) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. Handbook of X-Ray Photo-electron Spectroscopy; Perkin-Elmer Corp.: Eden Prairie, MN, 1979. (10) Tenne, R.; Hodes, G. Appl. Phys. Lett. 1980, 37, 428.

entry	thiol ^a (pH)	electrode	potential vs. SCE, V	% conversion (coulombs passed)	curr efficiency, ^b %	curr density, mA/cm ²	savings vs. Pt, ^c V
1	0.1 M cysteamine (pH 7.2)	n-CdS	-0.55	40 (50)	99	11.5	1.8
2	0.1 M 2-mercaptoethanol (pH 7.2)	n-CdS	-0.5	40 (80)	100	18	1.7
3	0.1 M penicillamine ^d (pH 7.2)	n-CdS	-0.7	78.5 (63)	98	13.5	1.9
4	0.1 M cysteine (pH 0.5)	n-CdS	-0.4	40 (53.5)	98	7.5	>2.0
5	1.0 M 2-mercaptoethanol (pH 11)	n-CdS	-0.7	16 (360)	98	20	1.2
6	1.0 M cysteamine (pH 11)	n-CdS	-1.0	3 (75)	96	17	1.0
7	0.5 M glutathione ^e (pH 0.5)	n-CdS	-0.4	33 (86)	59	10	>2.0
8	1.0 M 2-mercaptoethanol (pH 10.5)	n-CdSe	-0.6	40 (200)	97	10	1.1
9	1.0 M cysteamine (pH 10.5)	n-CdSe	-0.9	6 (151)	100	15	1.0

^a All solutions were 0.1 M Na₂SO₄. Adjustments in pH were made with NaOH or concentrated HCl. ^bBy HPLC; associated error is ±2%. ^cSavings refers to the difference in potential required to maintain a given current density at Pt and n-CdX. ^dPenicillamine = $(CH_3)_2C(SH)CH$ - $(NH_2)CO_2H$. Glutathione = HOOCCH(NH_2)CH_2CH_2(C=O)NHCH(CH_2SH)(C=O)NHCH_2CO_2H.

oxidation according to eq 4 is obtained at a current density of 20 mA/cm^2 . The same current density can be maintained at the illuminated n-CdS when the electrode potential is only -0.5 V vs. SCE. Thus, the light-driven oxidation of 2-mercaptoethanol to 2-hydroxyethyl disulfide at n-CdS allows a savings of 1.7 V of electrical driving force compared to a Pt electrode, without any sacrifice of rate or current efficiency. Such "savings" in electrical driving force, of course, depend on the nature of the dark electrode used. There are doubtless electrodes, for example, that are superior to Pt as an anode for the process represented by eq $4.^{11}$ It is probably best to discuss the value of the illuminated semiconductors with respect to the thermodynamic potentials associated with the RSSR/RSH redox couple. At pH 7.2, the formal potential, $E^{\circ\prime}$, of the 2-mercaptoethanol system is -0.46 V vs. SCE.¹² Thus, the photocurrent onset for n-CdS is more negative than $E^{\circ\prime}$, indicating that light can be used to drive the uphill oxidation process. The lack of current near $E^{\circ\prime}$ for a Pt anode shows extremely poor kinetics for the electrochemical process represented by eq 4 at Pt. Some quantitative measurements of efficiency of optical energy utilization are given below, but here it is worth noting that oxidation of RSH at the illuminated n-CdX can occur with apparent kinetics that are far superior to the kinetics at Pt.

Table I shows the results of controlled potential photoelectrochemical oxidations of several RSH at n-CdS and n-CdSe under a variety of conditions. The current efficiency for all entries was determined by HPLC, with the peak identities confirmed by comparison (retention time and UV-vis spectrum) to authentic samples. Figure 2 shows data for entry 8 in Table I, for example. Generally, the data in Table I show that a variety of RSH can be oxidized to RSSR with high current efficiency at illuminated n-CdX in acidic or basic solution. The notable exception is that glutathione is not photoelectrochemically oxidized with good current efficiency, possibly a consequence of product adsorption on the electrode surface. But in the other cases photoelectrochemical oxidation can be driven to substantial extent conversion and at high current density without deterioration in the current efficiency or decomposition of the n-CdX photoelectrode. The photoelectrodes used in the controlled potential electrolyses were typically of 0.1 cm² area. Thus, several thousand coulombs of charge per square centimeter can be passed through the semiconductor/solution interface without obvious difficulty. For the situations where the largest amount of charge was passed through the interface, there was enough charge passed to decompose the photoelectrode several times over, if the decomposition according to eq 1 occurred. With the exception of glutathione, there is no evidence of gross decomposition of the photoelectrode for any RSH used. We should note that other workers have concluded that certain thiols, including cysteine, are not capable of stabilizing

polycrystalline CdS with respect to photoanodic decomposition.² However, the likely key to achieving sustained photoelectrochemical oxidation is to keep the electrode potential as negative as possible. Generally, there is no photoanodic decomposition current at the potentials used even in the presence of innocent electrolytes; the observation of significant photocurrent in the presence of RSH/RS⁻ signals a favorable interaction of the RSH/RS⁻ with the CdX surface. The data in Table I are for electrodes held near the maximum power point in the photocurrent-voltage curves. The final generalization from data shown in Table I is that there is a significant voltage savings associated with the illuminated semiconductors compared to a Pt anode operated at the same current density.

In general the pH does not affect the ability of the n-CdX to give high current efficiency for the oxidation of RSH to RSSR, and the pH for the various systems in Table I is more or less arbitrary. However, for cysteamine and 2-mercaptoethanol note that data are included for pH 7.2 and pH 11 for oxidation at CdS. These data, entries 1, 2, 5, and 6, show that solutions that contain principally RSH or a large fraction of RS- will both give good current efficiency for the formation of RSSR. An important point, though, is that at high pH the photoelectrochemical oxidation can be sustained at high current density at values of $E_{\rm f}$ that are significantly negative of E_{FB} for CdS and CdSe in the presence of "innocent" electrolytes.¹⁴ This result suggests that the RS⁻ interacts with the CdX surface to shift E_{FB} to a more negative value. The effects of pH on the interface energetics will be elaborated below. The case of cysteine shows that high current efficiency can also be obtained in strongly acidic solutions. At pH 7.2 the cystine product precipitates onto the photoelectrode and blocks sustained photoelectrochemical oxidation, but at pH 0.5, precipitation of cystine is averted and a high efficiency oxidation can be effected, entry 4 of Table I. The kinetics of oxidation of the same cysteine solution at Pt are sufficiently poor that an anodic process leading to evolution of a gas, presumably O_2 , competes with the formation of cystine. A voltage savings in excess of 2 V can be realized by using the method of photoelectrochemical oxidation. Apparently, the current efficiency for formation of RSSR at the illuminated n-CdX does not depend on pH, but there are practical constraints in particular systems that preclude detailed, direct measurements of the current efficiency for a wide range of pH's.

Only in the case of glutathione is there a significant departure from the otherwise efficient formation of RSSR from RSH at illuminated n-CdX. Table I and Figure 3 give some data for the behavior of glutathione at CdS. When a n-CdS anode is irradiated in the presence of a pH 0.5/0.5 M solution of the cysteine-containing tripeptide glutathione (Table I, entry 7), a current efficiency of only about 60% is found for oxidized glutathione. Thus, approximately 40% of the photogenerated oxidizing equivalents corrode n-CdS, according to eq 1. The gradual yellowing of the solution during the photoelectrochemical oxidation of glutathione is consistent with decomposition of the photoanode. Direct evi-

⁽¹¹⁾ Zagal, J.; Fierro, C.; Rozas, R. J. Electroanal. Chem. 1981, 119, 403.

⁽¹¹⁾ Zagai, J.; Pierro, C.; Rozas, R. J. Electroanal. Chem. 1961, 119, 403. (12) (a) Szajewski, R. P.; Whitesides, G. M. J. Am. Chem. Soc. 1980, 102. (2011. (b) Patai, S., Ed. The Chemistry of The Thiol Group; Wiley: New York, 1974; Part II, p 787. (c) pK_a (cysteamine) = 10.75; pK_a (2-mercaptoethanol) = 9.6; pK_a (3-mercaptopropionic acid) = 10.6; pK_a (cys-teine) = 10.28; pK_a (glutathione) = 8.7. (13) Bard, A. J., Lund, H., Eds. Encyclopedia of Electrochemistry of the Elementic Maccol Dakker: New York, 1078; Vol. XII, pp. 202-411

Elements; Marcel Dekker: New York, 1978; Vol. XII, pp 393-411

⁽¹⁴⁾ Ellis, A. B.; Kaiser, S. W.; Bolts, J. M.; Wrighton, M. S. J. Am. Chem. Soc. 1977, 99, 2839



Figure 3. Scanning electron micrographs of (a, top) n-CdS after 1 min of photoetching (cf. ref 10 for procedure) in 12 M HCl; (b, middle) n-CdS after photoelectrolysis in a pH 11, 1 M cysteamine/0.1 M Na₂SO₄ solution for 20 h; (c, bottom) n-CdS after photoelectrolysis in a pH 11, 1 M glutathione/0.1 M Na₂SO₄ solution for 15 h.

dence of the inability of glutathione to suppress photoanodic decomposition of n-CdS is illustrated in Figure 3, which shows scanning electron micrographs of n-CdS after three different electrode treatments. The top picture shows a photoetched n-CdS; this treatment causes formation of a large number of submicrometer etch pits, giving a larger effective surface area and consequently, higher efficiency as a photoelectrode.¹⁰ The middle photograph is of an electrode used in the controlled potential photoelectrolysis of a pH 11/1 M cysteamine solution (Table I,



Figure 4. Auger electron spectra of (a) freshly etched n-CdSe (15 s in aqua regia, 5 min in concentrated KCN, H_2O rinse); (b) an n-CdSe electrode used in a controlled potential photoelectrolysis of 2-mercaptoethanol, with 200 C passed (Table I, entry 8); (c) an n-CdSe electrode used in controlled potential electrolysis of polysulfide, with 10 C passed. Electrode areas used in the photoelectrolyses were 0.1 cm².

entry 6). This electrode gives efficient cysteamine oxidation, and shows a morphology similar to that obtained by photoetching: complete coverage of the electrode surface with submicrometer etch pits. The bottom micrograph shows an n-CdS electrode after a controlled potential photoelectrolysis of 1.0 M glutathione solution at pH 11. In addition to the submicrometer etch pits seen in the other micrographs, large holes several micrometers in diameter are present, a clear indication of decomposition of the electrode. While photoelectrosynthesis of oxidized glutathione at n-CdS is far from an efficient process, we were unable to generate the same current density obtained for n-CdS at a Pt electrode at any potential short of gas evolution; apparently, irreversible adsorption of glutathione poisons the surface of the Pt electrode.

The final two entries in Table I demonstrate that n-CdSe is also an effective photoanode for formation of RSSR. From entry 9, it is seen that a pH 10.5 solution of 1 M cysteamine is oxidized to cystamine at n-CdSe irradiated with monochromatic 632.8-nm light with 100% current efficiency. Similarly, a solution of 2mercaptoethanol, Table I, entry 8, also gives a high efficiency for RSSR formation after passage of 200 C, enough charge to completely corrode the photoelectrode if decomposition occurred according to eq 1.

We were interested in the composition of the surface of CdSe electrodes used to produced RSSR from RSH/RS⁻, since previous work on single crystal n-CdSe indicates that in the presence of basic S_n^{2-} solution, extensive S/Se interchange occurs at the semiconductor surface, resulting in an amorphous or polycrystalline layer of CdS.¹⁵ Figure 4 shows the Auger sectra of n-CdSe after three different electrode treatments. The top spectrum shows an electrode immediately after an aqua regia etch and soak in KCN and H₂O. Apart from Cd, Se, and adventitious carbon, only Cl is seen, presumably a remnant of the aqua regia etching procedure.

^{(15) (}a) DeSilva, K. T. L.; Hareman, D. J. Electrochem. Soc. 1980, 127, 1554.
(b) Gerischer, H.; Gobrecht, J. Ber. Bunsenges. Phys. Chem. 1978, 82, 520.
(c) Cahen, D.; Hodes, G.; Manassen, J. J. Electrochem. Soc. 1978, 125, 1623.
(d) Noufi, R. N.; Kohl, P. A.; Rogers, J. W., Jr.; White, J. M.; Bard, A. J. J. Electrochem. Soc. 1979, 126, 949.

TABLE II: Output Parameters for 1 M Thiols at n-CdX^a

			light					
	$E^{\circ'},$		intensity,				$E_{V(oc)},$	
thiol	V vs. SCE ^o	electrode	mW/cm ²	$\phi_{e}{}^{c}$	η_{\max}	FF	V vs. SCE	
HSCH ₂ CH ₂ NH ₂ (cysteamine)	-0.67	CdSe	10	0.77	10.6	0.54	0.51	
			30	0.81	10.6	0.48	0.54	
		CdS	10	0.90	15.4	0.53	0.63	
			30	0.94	14.5	0.55	0.67	
HSCH ₂ CH ₂ OH (2-mercaptoethanol)	-0.60	CdSe	10	0.77	5.8	0.41	0.35	
			30	0.86	5.3	0.30	0.45	
		CdS	10	0.93	13.2	0.55	0.63	
			30	0.90	10.4	0.44	0.71	
HSCH ₂ CH ₂ CO ₂ H (3-mercaptopropionic acid)	-0.65^{d}	CdSe	10	0.24 (0.81)	0.7	0.05	0.24	
			30	0.26 (0.88)	0.4	0.10	0.33	
		CdS	10	0.93 (0.93)	7.4	0.35	0.57	
			30	0.82 (0.91)	4.5	0.53	0.60	
$HSCH_2CH_2CO_2Me$ (methyl-3-mercaptopropionate)	-0.65^{d}	CdSe	10	0.25 (0.82)	0.7	0.22	0.23	
			30	0.16 (0.89)	0.4	0.16	0.30	
		CdS	10	0.38 (0.93)	12.0	0.43	0.66	
			30	0.34 (0.85)	8.3	0.29	0.69	
HSCH2CHCO2H	-0.65	CdSe	10	0.80 (0.80)	4.0	0.17	0.50	
			30	0.67 (0.84)	2.1	0.11	0.56	
NH ₂		CdS	10	0.95 (0.95)	7.0	0.30	0.59	
(cysteine)			30	0.81 (0.90)	6.1	0.23	0.65	
HSCH ₂ CHCO ₂ Et	-0.65^{d}	CdSe	10	0.60 (0.93)	37	0.22	0.55	
	0100	0000	30	0.41(0.98)	1.8	0.16	0.53	
NHa		CdS	10	0.35 (0.86)	2.4	0.12	0.55	
(cysteine ethyl ester)			30	0.34 (0.84)	1.0	0.07	0.49	
dutathione	0.55	Casa	10	0.09 (0.92)	0.1	0.10	0.12	
grutatinone	-0.35	Cuse-	10	0.08(0.82)	0.1	0.10	0.13	
		CASE	30	0.00 (0.91)	1.5	0.07	0.17	
		Cus	10	0.09(0.88)	1.3	0.05	0.45	
			50	0.05 (0.90)	0.0	0.10	0.51	

^a All data are for pH 11/1 M thiol/1 M Na₂SO₄ aqueous solution with excitation at 501.7 nm for n-CdS and 632.8 nm for n-CdSe. See Figure 5 for steady-state photocurrent-voltage curves. ^b Calculated from data in ref 12. ^c Quantum yield for electron flow at $E^{\circ'}$. The values in parentheses are quantum yields for electron flow on the plateau of the photocurrent-voltage curves. Where there are no data in parentheses the quantum yields at $E^{\circ'}$ are the same as on the plateau of the photocurrent-voltage curves. ^d Values are assumed, since no literature data are available. ^eSustained energy conversion is not possible because the glutathione does not effectively suppress photoanodic decomposition of the photoelectrode.

The bottom spectrum is that of thoroughly rinsed n-CdSe after photoelectrolysis of a 1 M Na₂S/1 M S/1 M NaOH solution (-1.0 V, 10 mW/cm^2 , 100 C/cm^2 passed). The presence of the S peak is evidence for S/Se intercharge; the formation of CdS is confirmed by XPS data, which shows S in the -2 oxidation state. The middle spectrum is of the n-CdSe after use in the photoelectrochemical oxidation of 2-mercaptoethanol (Table I, entry 8). Though more than an order of magnitude more oxidizing equivalents reached the interface than for the oxidation of the S_n solution, the n-CdSe shows no evidence of S/Se exchange found for the electrode used in S_n^{2-} solution. Formation of n-CdS on n-CdSe in the presence of aqueous RSH solutions would require scission of a C-S bond, a process not consistent with the controlled potential photoelectrolysis data that show 100% efficiency for the formation of RSSR. However, the Auger electron spectroscopy can detect very small amounts of surface S. The absence of S in the Auger spectrum in the middle frame of Figure 4 shows that the RSH species are not desulfurized in the photoelectrochemical oxidation at illuminated n-CdSe.

Another point that can be made from the Auger spectrum for the electrode used for the photoelectrochemical oxidation of 2mercaptoethanol is that the RSH/RS⁻ system does not persistently adsorb to the electrode surface, as was found for $Et_2NCS_2^{-,1}$. While shifts in E_{FB} do signal adsorption of RS⁻ (vide infra), the ability to rinse the electrode free of S-containing material after exposure to the electrolyte solution shows that the RS⁻ is more easily removed than is the adsorbed $Et_2NCS_2^{-}$. However, a quantitative comparison of desorption rates has not been made.

Photocurrent-Voltage Curves for Oxidation of RSH/RS⁻ at n-CdX as a Function of R. Photoelectrochemical cells for conversion of optical energy based on the RSSR/RSH/RS⁻ redox system are potentially attractive in that the redox system is optically transparent in the region of interest for solar energy applications. The data from controlled potential electrolyses establish that the n-CdS photoelectrodes are rugged for several RSSR/ RSH/RS⁻ systems. Steady-state photocurrent-voltage curves,

however, show that there is considerable variation in the efficiency that can be achieved for the photoelectrochemical oxidation of the RSH/RS^{-} system, depending on the nature of R. Figure 5 illustrates the steady-state behavior of several RSH/RS⁻ systems at single crystals of n-CdS and n-CdSe. The data were obtained under identical conditions of light intensity (30 mW/cm²), scan rate (5 mV/s), and pH (11) for both semiconductors. At both photoanodes, there is an obvious difference in the shape of the power curves for each of the five RSH/RS⁻ systems. While the data shown are for single electrodes, it is important to point out that these results are representative of a large number of electrodes used. We have found essentially the same behavior at literally dozens of unpolished, freshly etched electrodes of both CdS and CdSe. In all cases, cysteamine and 2-mercaptoethanol give the "best" photocurrent-voltage curves, and glutathione gives the worst, with cysteine and 3-mercaptopropionic acid intermediate in behavior. Here "best" refers to the extent to which the curves are rectangular and have a negative onset of photocurrent to result in a high efficiency for the conversion of optical energy to electricity.

Table II summarizes the optical to electrical energy conversion efficiencies associated with the data given in Figure 5; data for the ethyl ester of cysteine and the methyl ester of 3-mercaptopropionic acid are included in Table II but are not included in Figure 5. The quantitative results show that CdS generally gives more efficient energy conversion than CdSe. As the photocurrent-voltage curves would suggest, there is considerable variation in the efficiency depending on the RSH/RS⁻ system used. In addition to the overall conversion efficiencies, calculated from eq 2, Table II gives other important parameters including the quantum yield for electron flow at short-circuit, the quantum yield on the plateau of the photocurrent-voltage curve, and the fill factor, FF, defined by eq 5 where i_{sc} is the photocurrent at $E_f =$

ill factor =
$$[(iE_V)_{max}/(E_{V(oc)}i_{sc})]$$
 (5)

 $E_{\rm redox}$. The fill factor is generally regarded as the quantitative



Figure 5. Steady-state photocurrent-voltage curves (5 mV/s) in the presence of 1 M RSH/0.1 M Na₂SO₄ at pH 11 for various R- groups at (a) n-CdSe irradiated at 632.8 nm at 30 mW/cm² and (b) n-CdS irradiated at 501.7 nm at 30 mW/cm². Energy conversion parameters are summarized in Table II.

measure of the rectangularity of photocurrent-voltage curves.

Two experiments demonstrate that the differences in the properties of the RSH/RS⁻ systems, rather than in any properties of the RSSR molecules formed, are responsible for the observed variations in the photocurrent-voltage curves and efficiencies for the seven RSSR/RSH/RS⁻ systems. The first is that addition of 0.1 M of the corresponding RSSR has no effect on the shape of the photocurrent-voltage curves for a given RSH/RS⁻ system. Indeed, addition of any RSSR has essentially no effect. The second experiment of interest concerns cysteine and shows that moving to pH 14, where cysteine has a much higher solubility than at pH 11, does not substantially alter the cysteine photocurrent-voltage curve. These two experiments allow us to focus on the properties of RSH/RS⁻ to rationalize the differences in the shapes of the photocurrent-voltage curves in Figure 5.

Three features of the seven RSSR/RSH/RS⁻ systems are very similar. First, with the exception of the glutathione, each system is effective in suppressing the photoanodic decomposition of the n-CdX, and RSH/RS⁻ is converted to RSSR with high current efficiency. Second, the pK_a 's of the RSH molecules studied are all below 11,¹² so that in every case, the RS⁻ form is the principal electrochemically active species in solution. Third, with the exception of glutathione ($E^{\circ\prime}$ (pH 11) = -0.55 V vs. SCE), the pH 11 redox potentials of the molecules are very similar, falling in the range -0.60 to -0.67 V vs. SCE.¹² Another, perhaps less relevant, fact is that the limiting current is found to be near 11 mA/cm² at 30 mW/cm² at both n-CdS and n-CdSe in every case. Thus, the limiting quantum yield for electron flow is the same for all RSH/RS⁻. We take the limiting current to be the current found at the plateau of the photocurrent-voltage curve (where the current is found to be potential-independent). This fact may be less relevant than the first three because one might expect the photocurrent to become limited by the excitation rate at sufficiently positive potentials no matter what species are in the solution. The key is that nearly unit quantum yield for electron flow is expected when the band bending is sufficiently great (to inhibit back reaction). However, the point that can be made is that the RSH/RS⁻ species do not themselves adsorb and block the surface, at least when the potential is sufficiently positive. Despite these similarities of the RSH/RS⁻ systems there are differences among them that give apparent changes in the kinetics for the formation of RSSR.

The data in Table II show that the overall energy conversion efficiencies for the RSH/RS⁻ systems vary by more than an order of magnitude, ignoring the glutathione system for which sustained energy conversion cannot be claimed, because the photoelectrodes are grossly corroded when irradiated in the presence of glutathione. The highest efficiency of any system investigated is attained at n-CdS for a 1 M cysteamine solution, which gave an energy conversion efficiency of 14.5% at 30 mW/cm² and 15.4% at 10 mW/cm^2 . While the potential for photocurrent onset among the RSH/RS⁻ investigated deviates most significantly for glutathione. the value of $E_{V(\infty)}$ even for this system does not appear much smaller, owing to the more positive $E^{\circ'}$. The largest photovoltages obtained are for n-CdS, with cysteamine giving 670 mV and 2-mercaptoethanol giving over 700 mV. The dramatic difference in behavior of two RSH/RS⁻ systems with similar structure and electrochemical properties is best illustrated by cysteamine and cysteine: the redox potentials of these molecules differ by only 20 mV, $E_{V(\infty)}$ values at n-CdS at 30 mW/cm² only differ by 20 mV, and yet the fill factor and η_{max} for cysteamine are more than double those for cysteine. Clearly, removal of the carboxylate group of cysteine (to give cysteamine) has an enormously favorable effect on the electrochemistry at CdS and CdSe. The data for the ethyl ester of cysteine shows that the presence of the carboxylate functional group is not in itself detrimental, since the ethyl ester gives lower efficiency than the parent cysteine. However, the esterification of a carboxylate does not always give lower efficiency, since the methyl ester of 3-mercaptopropionic acid actually gives a higher efficiency than the parent acid at n-CdS. There appear to be no simple rationalizations for the wide range of efficiencies found for the various RSH/RS⁻ systems that are capable of effectively suppressing the decomposition of the n-CdX.

Variation in the rate of one or more of the fundamental steps in the net process represented by eq 3 could account for the variation in the energy conversion efficiencies given in Table II. We hypothesize that the variation in the efficiencies are due to variations in the rate of coupling of two, electrode bound, RS' species that are formed by h⁺ transfer to a RSH or RS⁻ species. This hypothesis accommodates the fact that there are big differences between CdS and CdSe; the strength of the interaction of RS[•] should depend on the nature of the surface. This hypothesis is also consistent with the fact that very subtle changes in the nature of R give rise to large variations in the photocurrent-voltage curves and efficiencies, because interaction of the R group with the CdX may control the rate of coupling. Whenever the coupling of RS' species is slow there is the prospect that there may be net electron-hole recombination at a given value of E_f resulting in little or no net photocurrent, even though the primary event of h⁺ capture is efficient. The result of slow coupling would be that the surface of the photoelectrode is covered with a layer of RS[•] that blocks net flow of current at the smaller band bending associated with large values of photovoltage. Furthermore, the band edges may shift to more positive values since the surface coverage of RS⁻ is reduced (vide infra). The fact remains, though, that we see little to guide us in the selection of R for the RSSR/ RSH/RS⁻ redox systems other than the empirical results provided in Table II and Figure 5.

Another issue deserves mention in connection with the conversion of optical energy to electricity using the RSSR/RSH/RS⁻ redox systems: an efficient device for electricity generation would require the development of a "good" counter electrode for the reduction process represented by eq 6. Electrodes do not exist

$$RSSR + 2e^{-} \rightleftharpoons 2RS^{-} \tag{6}$$

that will effect the reduction represented by eq 6 with small overvoltage, for any choice of R^{-13} Research is under way in this laboratory to evaluate the kinetics for the reduction at various



Figure 6. Plots of onset potential for photoanodic current vs. pH at n-CdS (30 mW/cm², 501.7-nm irradiation) for (a) 1 M cysteine/0.1 M Na₂SO₄; (b) 1 M 2-mercaptoethanol/0.1 M Na₂SO₄; (c) 1 M cysteamine/0.1 M Na₂SO₄. Circles refer to the Cd-rich face, and x's to the S-rich face of the CdS.

electrodes and to attempt to catalyze the process represented by eq 6.

As noted above, the n-CdX photoanodes for formation of RSSR operate at a substantial voltage savings compared to Pt anodes, at a given current density. The data in Table II give the thermodynamic efficiencies that are needed to make predictions regarding utility of the n-CdX photoelectrodes if the objective were to convert light to electricity. However, if the objective is to use the photoelectrochemical method for synthetic purposes, the comparison of the n-CdX anodes under illumination and conventional electrodes needs to be made. In this situation the utility of the n-CdX must be evaluated not on the basis of the predicted energy conversion efficiency, but on the actual energy saved considering that there will be greater and lesser overvoltages depending on the rates (currents) needed and on the actual electrode used. While the illuminated n-CdX electrodes appear to represent a real advantage compared to Pt, even considering that light must be used, it is not at all clear that the photoelectrochemical approach is the optimum. There are likely far better electrodes than Pt for the oxidation of RSH/RS⁻¹

Electrochemical Behavior of RSH/RS⁻ at n-CdX as a Function of pH. Since the photocurrent onsets at n-CdS and n-CdSe in the presence of pH 11/1 M RSH/RS⁻ solutions are significantly negative of the known values of $E_{\rm FB}$ for CdS and CdSe in the presence of innocent electrolytes, we have undertaken studies to establish that RS⁻ adsorption is responsible for the shift in $E_{\rm FB}$. In Figure 6, we show the shift in $E_{V(\infty)}$ with pH for 1 M solutions of cysteine, 2-mercaptoethanol, and cysteamine at n-CdS. Given that the band edges of n-CdS are fixed from pH 0 to pH 14 in innocent electrolytes (vide infra), the shift in $E_{V(\infty)}$ can be related directly to the deprotonation of RSH to form RS⁻. For these RSH/RS⁻ systems we see large (up to about 600 mV) negative shifts in potential for onset of photoanodic current at the higher pH values. For this study we examined both the S- and Cd-rich single-crystal faces of the CdS oriented with the c axis perpendicular to the face. The S-rich face consistently gives slightly more negative onsets than the Cd-rich face, but in essence the results are independent of the face. The curves all have sigmoidal shapes, with the onset potential for photoanodic current vs. pH showing an inflection point at a pH consistent with the pK_a of the RSH molecules. The conclusion is that the RS⁻ is responsible for the shift in the onset potential of photoanodic current. Our results differ somewhat from those reported previously² for cysteine in that we observe only one inflection in the plot of E_{FB} vs. pH. The earlier work involved the use of polycrystalline CdS, and the -COO⁻ group of the cysteine was proposed to be adsorbed. It is possible that the polycrystalline CdS has oxide sites for interaction with the -COO⁻ that are not present on the single-crystal material. It should be pointed out that the polycrystalline material also shows a shift of $E_{\rm FB}$ with variation in pH that we do not find for the single-crystal samples used in our work (vide infra). It should also be noted that we obtain the same shape for the curve for 2-mercaptoethanol as for cysteine. The cysteine is potentially complicated by the various acid-base equilibria possible, but the 2-mercaptoethanol involves only the RSH/RS⁻ species in the pH regime investigated.

Differential capacitance measurements support the hypothesis that RS^- adsorption is responsible for shifts in E_{FB} at n-CdX. Generally, the onset potential for photoanodic current corresponds closely to the value of E_{FB} , but measurement of the interface capacitance is regarded as a better way to determine E_{FB} when there are kinetic problems as there are with the RSH/RS⁻ systems. Through the Mott–Schottky relation, eq 7, we have determined

$$[C_{\rm sc}]^{-2} = 2[-(E_{\rm f} - E_{\rm FB}) - kT/e]/(e\epsilon\epsilon_0 e)$$
(7)

the $E_{\rm FB}$ of n-CdX in the presence of thiols. In eq 7, *n* is the donor density, ϵ is the semiconductor dielectric constant, ϵ_0 is the permittivity of free space, and *e* is the electronic charge.⁷ The literature values for ϵ are 5.4 and 10 for n-CdS and CdSe, respectively.¹⁶ We have observed ideal Mott-Schottky behavior (linear plots of $[C_{\rm sc}]^{-2}$ vs. $E_{\rm f}$ having the same slope and intercept at frequencies from 500 Hz to 10 kHz) for CdS and CdSe exposed to various RSH/RS⁻ solutions. The intercept of the Mott-Schottky plots gives the value of $E_{\rm FB}$.

It is generally accepted that shifts of $E_{\rm FB}$ of a semiconductor in electrolyte solutions are a consequence of strong adsorption of solution species onto the semiconductor resulting in excess charge in the Helmholtz layer. This phenomenon has been carefully examined in the case of sulfide adsorption on n-CdS.¹⁷ In some cases, adsorption of $OH^{\scriptscriptstyle -}$ has been found to shift the band edges of single crystal n-CdX.¹⁸ For this reason, we have determined, by capacitance measurements, E_{FB} for the Cd-rich, (0001) face of n-CdS in 0.1 M Na₂SO₄ from pH 0 to 14. The linear Mott-Schottky plots we obtained at frequencies between 500 Hz and 10 kHz give the same intercept of -0.90 V vs. SCE. The lack of pH dependence of E_{FB} of the Cd-rich face of (0001) n-CdS agrees with previously published data for the same material.¹⁹ We find the same results with n-CdSe, with $E_{\rm FB} = -0.70$ V vs. SCE.¹⁴ Thus, any shifts of $E_{\rm FB}$ observed with these materials can be attributed to the presence of adsorbed species not involving the H_2O/OH^- system.

Figure 7 shows the Mott-Schottky plots for 1 M RSH/RS⁻/0.1 M Na₂SO₄ at low pH (1.5) and high pH (11) at n-CdSe. First, we note the large negative shifts in E_{FB} at the high pH for the RSH/RS⁻ shown, about 650 mV. Second, the lines are all parallel indicating that no change in donor density has occurred. Since

⁽¹⁶⁾ Sze, S. M. Physics of Semiconductor Devices; Wiley: New York, 1981.

⁽¹⁷⁾ Ginley, D. S.; Butler, M. A. J. Electrochem. Soc. 1978, 125, 1968.
(18) Frese, K. W., Jr.; Canfield, D. G. J. Electrochem. Soc. 1984, 131, 2614.

⁽¹⁹⁾ Watanabe, T.; Fujishima, A.; Honda, K. Chem. Lett. 1974, 897.



Figure 7. Plots of $1/C_{sc}^2$ vs. potential (Mott-Schottky plots) for 1 M RSH/RS⁻/0.1 M Na₂SO₄ solutions at pH 1.5 and pH 11 at n-CdSe: (a) cysteine, (b) mercaptoethanol, (c) cysteamine.

TABLE III: Values of E_{FB} for 1 M Thiol Solutions at Low and High pH at n-CdS and n-CdSe^a

			$E_{\rm FB}$		
thiol	electrode	pН	V vs. SCE	ΔE_{FB} , V	
HSCH ₂ CH ₂ NH ₂	n-CdS	1.5	-0.89		
		11	-1.41	0.52	
	n-CdSe	1.5	-0.66		
		11	-1.30	0.64	
HSCH ₂ CH ₂ OH	n-CdS	1.5	-0.90		
		11	-1.25	0.35	
	n-CdSe	1.5	-0.70		
		11	-1.41	0.71	
HSCH ₂ CHCO ₂ H	n-CdS	1.5	-0.88		
		11	-1.28	0.40	
NH2	n-CdSe	1.5	-0.73		
-		11	-1.28	0.55	
glutathione	n-CdS	1.5	-0.90		
		11	-1.16	0.26	
	n-CdSe	1.5	-0.80		
		11	-1.36	0.56	

 ${}^{a}E_{\rm FB}$ values were determined from the intercepts of Mott-Schottky plots, cf. Figure 7. All solutions were 0.1 M in Na₂SO₄. The estimated absolute error is 50 mV, but differences in $E_{\rm FB}$ have an estimated error of less than 20 mV.

we have shown that pH by itself does not shift $E_{\rm FB}$ of n-CdSe, the RS⁻ ion formed at above pH 10 must be responsible for the shift in $E_{\rm FB}$, as also concluded from the data in Figure 6. Table III presents the $E_{\rm FB}$ values at high and low pH for 1 M solutions of cysteamine, 2-mercaptoethanol, cysteine, and glutathione at n-CdS and n-CdSe. At n-CdSe, we note that all RSH/RS⁻ at low pH yield an $E_{\rm FB}$ of about -0.70 V vs. SCE. At n-CdS, we find that all thiols at low pH yield an $E_{\rm FB}$ of about -0.90 V vs.



Figure 8. Plots of $1/C_{sc}^2$ vs. E_f (Mott-Schottky plots) for various concentrations of RS⁻ at pH 14 at n-CdS: (a) cysteamine, (b) glutathione.

TABLE IV: Thiol Concentration Effect on E_{FB} of CdS at pH 14

thiol	concn, mM	E _{FB} , V vs. SCE
glutathione	0	-0.93
	50	-1.02
	100	-1.07
	150	-1.11
	200	-1.14
cysteamine	0	-0.93
	20	-1.07
	50	-1.25
	73	-1.35
	100	-1.38
	150	-1.42
cysteine	0	-0.90
	25	-1.04
	50	-1.12
	100	-1.17
	150	-1.20
	200	-1.23
2-mercaptoethanol	0	-0.91
	25	-1.06
	50	-1.09
	100	-1.16
	150	-1.18
	200	-1.20

 a Conditions are as for the data in Table III. Data for glutathione and cysteamine are plotted in Figure 9.

SCE, the same $E_{\rm FB}$ value for n-CdS in innocent electrolytes. The low pH $E_{\rm FB}$ values show that specific adsorption of charged species does not occur in solutions of RSH. However, large negative shifts of $E_{\rm FB}$ are found at high pH, but the magnitude of the shift depends on the semiconductor and on the particular RS⁻. For CdSe the largest $E_{\rm FB}$ shift occurs with 2-mercaptoethanol, about 710 mV, while the smallest $E_{\rm FB}$ shift occurs with glutathione, about 560 mV. For CdS the largest shift in $E_{\rm FB}$ is seen with cysteamine, 520 mV, while the smallest shift is seen with glutathione, 260 mV.

The variation in $E_{\rm FB}$ of CdS with variation of the concentration of the RSH/RS⁻ system was studied for some of the systems. Figure 8 shows Mott-Schottky plots for various concentrations of cysteamine and glutathione at pH 14, and Table IV summarizes the data for the four systems studied. As in our related article



Figure 9. Plots of ΔE_{FB} of n-CdS vs. solution thiol concentration for cysteamine and glutathione at (a) pH 7.2 and (b) pH 14.

on the interaction of the dithiocarbamates,¹ we note that the Mott-Schottky plots at different concentrations of RS⁻ are parallel. The figure shows that, at pH 14, 20 mM cysteamine shifts $E_{\rm FB}$ 125 mV more negative than 200 mM glutathione. Moreover, if we relate the shift in $E_{\rm FB}$ to the coverage of the adsorbate,¹ the data show that the cysteamine reaches its saturation surface coverage at a somewhat lower bulk concentration than the glutathione, as illustrated by the plots of $E_{\rm FB}$ shifts vs. concentration of the RSH/RS⁻ system in Figure 9. It is thus certain that the interaction of glutathione. This larger interaction for cysteamine correlates with the superior photoelectrochemical behavior of cysteamine, compared to glutathione, at n-CdS.

Figure 9 shows the plots of $E_{\rm FB}$ for CdS vs. RSH/RS⁻ concentration for both pH 7.2 and 14 for cysteamine and glutathione. We note that overall $E_{\rm FB}$ shifts are much smaller at pH 7.2 than at pH 14, which is consistent with the low concentration of RS⁻ ions (compared to the RSH form) at pH 7.2. What is interesting about these data is that the shift in $E_{\rm FB}$ levels off at pH 7.2 at about the same total concentration of RSH/RS⁻ as at pH 14 where only the RS⁻ form is present. The point is that increasing the total RSH/RS⁻ concentration at pH 7.2 should continue to raise the amount of the adsorbing anionic species to a value sufficient to shift the value of $E_{\rm FB}$ to the most negative extent found at pH 14. The data suggest that the neutral RSH form interacts strongly with the surface and blocks the RS⁻ from the surface, but since it is not charged does not result in a shift in E_{FB} . If we view the interaction of the RS⁻ as a ligand toward a Cd site it is not surprising that RSH could be bound also. The bound

RSH/RS⁻ system would then give a shift in E_{FB} at pH 7.2 governed, in part, by the pK_a of the bound system. Given that the RSH form can be efficiently photoelectrochemically oxidized, it is not surprising that a strong interaction of the RSH with the surface would be found.

The concentration dependence of the shifts in $E_{\rm FB}$ in the RS⁻ systems studied are summarized by the data in Table IV and Figures 8 and 9. While all systems show a general dependence that is consistent with more adsorption at higher concentration of the adsorbing species and a saturation in coverage at concentrations above some value, the curves do not fit simple Langmuir adsorption isotherms as found for the dithiocarbamates in CH₃CN/electrolyte solution.¹ Thus, detailed analysis of the adsorption is not easy. However, some qualitative statements can be made from the pH 14 data given in Table IV. First, in comparison to results for the dithiocarbamates studied in $CH_3CN/$ electrolyte, the RS⁻ systems in aqueous electrolytes must be at a substantially higher concentration in order to achieve the maximum shift in $E_{\rm FB}$. For the four systems studied concentration in excess of 0.1 M is required in order to achieve the saturation shift, whereas the most weakly bound dithiocarbamate requires only about 4 mM bulk concentration in order to achieve its saturation coverage. Second, as for the dithiocarbamates, the adsorption of RS⁻ appears to be strong enough that relatively negative values of $E_{\rm F}$ can be used throughout a photoelectrochemical oxidation to a large fractional conversion to RSSR that does not interact with the surface. Third, the advantage realized by adsorption of the RS⁻ in aqueous electrolyte is somewhat clouded by the fact that the redox potential of the RSSR/ RSH/RS⁻ system is pH-dependent as is the adsorption, Figures 6 and 9. However, given the tendency of all n-type semiconductors to undergo photoanodic decomposition, there appears to be a general advantage in being able to use the most negative value of $E_{\rm f}$ possible for photoelectrochemical oxidation processes. Finally, considering the differences in the overall energy conversion efficiencies, Table II, for the four systems shown in Table IV the sensitivity of $E_{\rm FB}$ to variations in concentration are fairly similar for the four systems. We had hoped to be able to see substantial variations in the concentration dependence with variation in R. We speculate that adsorption in nonaqueous media will provide better insight into the behavior of the RS⁻, and work is now underway in these laboratories to attempt to understand the detailed aspects of RS⁻ adsorption by investigations carried out in nonaqueous media where, based on the results with dithiocarbamates,¹ simpler adsorption behavior may be found.

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Registry No. Cysteamine, 60-23-1; 2-mercaptoethanol, 60-24-2; penicillamine, 52-67-5; cysteine, 52-90-4; penicillamine anion, 41079-68-9; glutathione, 70-18-8; cysteamine disulfide, 51-85-4; 2-mercapto-ethanol disulfide, 1892-29-1; penicillamine disulfide, 20902-45-8; cysteine disulfide, 56-89-3; glutathione disulfide, 27025-41-8; 3-mercaptopropionic acid, 107-96-0; methyl 3-mercaptopropionate, 2935-90-2; cysteine ethyl ester, 3411-58-3; glutathione anion, 52993-47-2; cysteamine anion, 1492-51-9; cysteine anion, 19237-87-7; 2-mercaptoethanol anion, 57966-62-8; CdS, 1306-23-6; CdSe, 1306-24-7; Na₂SO₄, 7757-82-6.