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Photoelectrochemistry of Cadmium Sulfide. 1. Reanalysis of Photocorrosion and Flat-Band Potential

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The photoelectrochemical behavior of cadmium sulfide depends strongly on the pretreatment of the electrodes. Sulfur, the main photocorrosion product of CdS, changes the potential drop across the Helmholtz double layer and shifts the flat-band potential of CdS in the anodic direction. Removal of sulfur from the surface is possible by prepolarizing the electrode at about -1.1 V(SCE) in the presence of oxygen. The flat-band potential of the clean (0001) Cd surface has been determined to about -1.8 V(SCE) in the dark. Illumination of the electrode leads to surface-state charging due to formation of S^{2-} , the intermediate in the formation of both possible photooxidation products: S^0 in the absence of oxygen and SO_4^{2-} in the presence of oxygen.

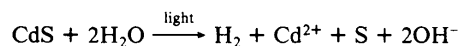
Introduction

Cadmium sulfide is one of the best characterized semiconductors for use in solar-energy conversion systems. Far more than 500 papers concerning the photophysical and photochemical behavior of this material have been published. One main reason for the interest in this material is the position of the band edges in aqueous solution, which is believed to be more suitable than that of nearly all other known semiconductors for the direct splitting of water into hydrogen and oxygen by solar energy,¹ which is the main goal of many photochemists and photoelectrochemists.²

According to the literature the flat-band potential of CdS in aqueous solution seems to be ideal for the water-splitting reaction. The position of the conduction band at the surface of CdS is located at sufficiently cathodic potential to reduce water if a catalyst is used to reduce the overpotential of this reaction. Hydrogen evolution from CdS is easy to observe, as has been proven many times.³ Furthermore, the reported flat-band position of CdS means that there should be a sufficient overpotential for holes in the valence band to oxidize water. Oxygen production from CdS has indeed been reported a few times.⁴ However, the

stoichiometric production of hydrogen and oxygen from catalyst-loaded CdS reported by Grätzel and co-workers^{4a} was surprising, especially because this meant a complete suppression of the CdS photocorrosion.

Our own attempts to split water using catalyst-loaded particles,⁵ monograin membranes,⁶ or electrodes⁷ failed completely: no oxygen was evolved. Depositing catalysts on cadmium sulfide exclusively caused an increase of photocorrosion by accelerating the rate of hydrogen production.⁸ However, in several experiments the amount of Cd^{2+} found in the electrolyte after the experiment remained less than that calculated by assuming the well-known photocorrosion reaction



In addition the pH increase expected for this reaction was never achieved when air was allowed to get into the cell. These dis-

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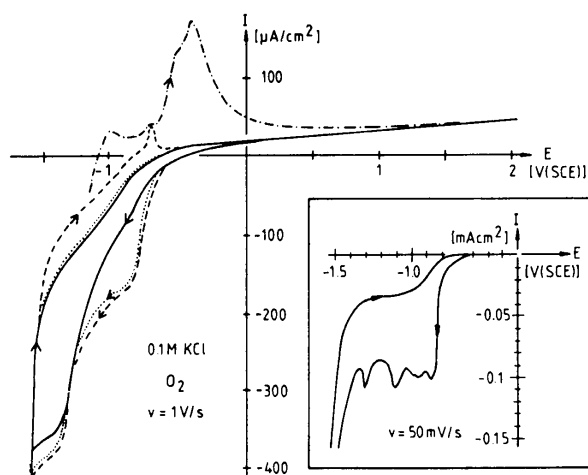


Figure 1. Dark currents at CdS in oxygen-saturated 0.1 M KCl solution: (—) polished and etched; (···) 5-min prepolarization at +2 V(SCE) in the dark; (---) 2- and (---) 10-s photooxidation at +2 V(SCE) (0.4 mA/cm²). Insert: slower scan rate, illuminated at 0 V(SCE) just before the scan.

crepancies and some other peculiarities initiated a reanalysis of the mechanism of photocorrosion and charge-transfer processes at CdS electrodes, the results of which are reported here.

Experimental Section

Cadmium sulfide electrodes were cut perpendicular to the *c* axis from single crystals purchased from Eagle-Pitcher Ind. The electrodes were provided on one side with ohmic contacts by use of indium (heated to 400 °C in a hydrogen stream for 4 h) and glued onto a contact screw with silver epoxy. After being molded with Scandiplast in Teflon holders, the surface was polished with diamond powder of decreasing size down to less than 0.5 μm to get mirrorlike surfaces. Before the experiments the electrodes were etched for 5 s in 20% HCl.

The electrochemical experiments were performed in a standard photoelectrochemical cell with anode and cathode compartments separated by an ion-exchange membrane (Nafion) if necessary. Saturated calomel electrodes prepared from KCl or NaCl were used as reference electrodes. The electrode potentials given in this paper are given with respect to the saturated calomel electrode (SCE). All chemicals used were analytical grade. Electrolytes were prepared from double-distilled water by using KCl, Na₂SO₄, or NaClO₄. RuO₂ and platinum were deposited by photodecomposition of RuO₄ and H₂PtCl₆, respectively (compare ref 4a). Purified nitrogen was used to flush the electrolyte for more than 15 min in experiments where oxygen had to be absent. Capacity measurements were done dynamically by using a fast lock-in amplifier (Ithaco Dynatrec 393) with potential scan rates up to 1 V/s.

Experiments under complete oxygen exclusion were performed in an argon- or helium-flushed glovebox. Hydrogen, oxygen, and nitrogen (from air) were analyzed by using a gas chromatograph (Shimadzu 6GC2-A1) inside the glovebox (conditions as in ref 9).

Results

Dark-Current Behavior. Freshly polished and etched electrodes in oxygen-containing electrolytes show relatively high dark currents at anodic potentials (more than 50 μA/cm² at +2 V(SCE)). Cathodic currents start at about -0.7 V(SCE), leading to two reduction peaks, the sizes of which strongly depend on the pretreatment of the electrodes and the oxygen content in the solution (Figure 1). Illumination of the electrodes as well as anodic prepolarization leads to an increase of the reduction currents. In addition, anodic oxidation peaks occur between -1.0 and -0.3 V(SCE), the heights and potentials of which depend on the amount

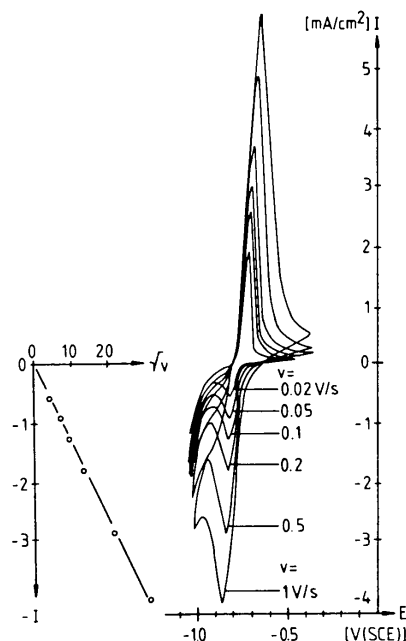


Figure 2. Cyclic voltammetry of Cd/Cd²⁺ at CdS using different scan rates (*v*) and plot of *I* versus *v*^{1/2} of the cathodic peak current density (0.1 M K₂SO₄, 10 mM CdSO₄).

of previous anodic corrosion, the amount of oxygen dissolved in the electrolyte, and the time of cathodic polarization at potentials negative of -0.9 V(SCE). The peak potentials are scan-rate dependent, and the peaks broaden and shift with longer photocorrosion times and thus higher coverage of the surface with sulfur and higher concentration of cadmium ions in the solution. Their reproducibility is poor. Slower scan rates also allow resolution of additional reduction peaks at potentials between -0.7 and -1.4 V(SCE) by using freshly oxidized electrodes (compare insert in Figure 1).

If a Cd²⁺ salt is added to the solution, a reduction peak at -0.9 V(SCE) and a corresponding anodic oxidation peak at -0.75 V(SCE) are seen as reported previously.¹⁰ Accordingly, these two single peaks are due to deposition and stripping of dissolved cadmium ions. The reduction of dissolved Cd²⁺ ions is diffusion controlled (peak height is proportional to the square root of the scan rate) as shown in the insert of Figure 2. The current/potential behavior in cyclic voltammetry as shown in this figure demonstrates in addition that an ohmic contact is formed to the cadmium metal, allowing a stripping of the metal at potentials only slightly anodic of the deposition potential.

A comparison of the much more complex current/voltage curves shown in Figure 1 with the rather simple deposition/stripping behavior of Figure 2 shows that additional reduction and oxidation reactions occur following the photocorrosion of CdS. We attribute them to the reduction and further oxidation, respectively, of sulfur and sulfur/oxygen species deposited on the surface during the photocorrosion reactions.

Prepolarization at potentials negative of -1.4 V(SCE) leads to the appearance of an oxidation peak at -0.7 V(SCE) even without previous anodic corrosion or addition of Cd²⁺ to the solution. This is attributed to cathodic lattice decomposition at very negative potentials. The anodic stripping of the Cd⁰ formed leads to Cd²⁺ in the solution. After this peak a related reduction peak at about -0.9 V(SCE) occurs. Cyclic potential scans reproduce the current/potential behavior shown in Figure 2. Long polarization times at potentials negative of -1.4 V(SCE) finally lead to an irreversible change of the electrode behavior, which now gives high anodic dark currents with ohmic potential de-

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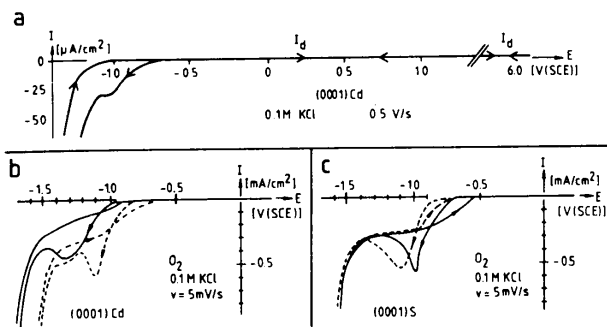


Figure 3. Dark currents at CdS in oxygen-saturated 0.1 M KCl solution after careful polishing, only short etching, and prepolarizing the electrodes at -1.1 V(SCE) in oxygen-containing solution (solid lines) and after photooxidation with 5 mA s (dashed line): (a) fast; (b and c) slow scans, exposing different faces to the electrolyte.

pendence. A gray highly conductive surface layer of cadmium metal can be seen. Thus the cathodic decomposition of CdS starts negative of about -1.4 V(SCE) as reported previously.¹¹

Careful polishing, only brief etching (about 5 s in 20% HCl), and prepolarization at a potential where oxygen dissolved in the electrolyte is reduced (at about -1.1 V(SCE)) lead to a drastically improved electrode behavior, as shown in Figure 3. Only very low dark currents (less than $5 \mu\text{A}/\text{cm}^2$) are seen even at anodic potentials as high as $+10$ V(SCE) (Figure 3a). Oxygen reduction now leads to a new single reduction step or peak, depending on the scan rate, the onset potential of which is dependent on the crystal plane used. At the CdS (0001) Cd surface, the oxygen reduction with slow scan rates starts at about -0.9 V(SCE) (Figure 3b), whereas it starts already at about -0.7 V(SCE) at the (0001) S surface (Figure 3c). Short photooxidation or longer anodic prepolarization leads to a shift of these onset potentials and by this to disappearance of the difference between the two crystal planes.

The change in electrode behavior during cathodic current flow can best be followed by cycling a polished and etched electrode (only 5 s in diluted HCl) between about -1.3 and $+0.5$ V(SCE) in oxygen-flushed solution, as shown in Figure 4. Only small cathodic currents—which are smaller the longer the etching was done—increase with the first few cycles. A well-defined reduction step or peak, depending on the scan rate, evolves, which stabilizes within about 1 h. After this time the current/potential behavior remains reproducible for hours. However, it changes immediately if the electrode is illuminated as described above.¹¹

Hydrogen production and the cathodic decomposition of CdS start at about -1.4 V(SCE) on both (0001) surfaces. The reduction of several dissolved species starts at about the same potential as the oxygen reduction (i.e., around -0.8 V(SCE)).¹² Deposition of metallic catalysts like platinum or RuO_2 shifts the onset potential of both the oxygen reduction as well as the hydrogen production by about 0.45 V in anodic direction (compare ref 7b).

The electrolyte was chemically analyzed after a certain amount of reduction current was passed through the electrode at potentials where the oxygen reduction just started ($I = I_{\text{diff}}/3$) and where it is diffusion controlled ($I = I_{\text{diff}}$). This analysis showed quantitative formation of OH^- for both pure CdS and CdS/ RuO_2 . No peroxide has been detected. Moreover, adding peroxide to nitrogen-flushed electrolytes led to exactly the same diffusion-controlled reduction step (I proportional to the concentration c) as seen with oxygen. No differences in the onset potential have been detected.

Capacity Measurements. Dynamic capacity measurements in the usual potential range between -0.5 and $+1.5$ V(SCE) lead

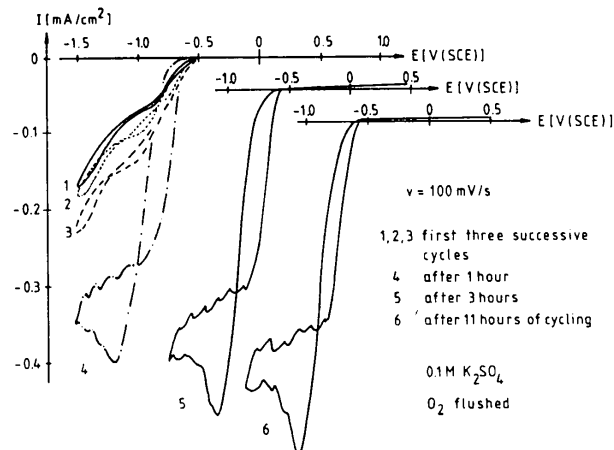


Figure 4. Improvement of electrode behavior of cycling the electrode potential in oxygen-bubbled 0.1 M K_2SO_4 solution: (1–3) first three cycles; (4) after 1 h, (5) after 3 h; (6) 11 h of cycling.

to straight Mott/Schottky plots with varying slopes and intersections with the x axis depending on the scan rate, the prepolarization potential, and the frequency of the measurement. Very different plots are obtained from electrodes after changing the chemical pretreatment, i.e., changing the etching times, rinsing the electrode with polysulfide solution, or illuminating the surface. With electrodes prepolarized in oxygen-flushed solution at -1.1 V(SCE) as described above, which suppressed the anodic dark currents to very low values, it was possible to extend the range of the measurement to more anodic potentials. Capacity measurements over more than 10 V thus became possible.

Figure 5 compares Mott/Schottky plots obtained from an electrode polished and etched as described in the literature (30 s in concentrated HCl (a)) with those of another electrode (b) that was polished, carefully etched (5 s in 20% HCl), and prepolarized at -1.1 V(SCE) in oxygen-containing solution as described above. Capacity measurements over the wider potential range reveal that electrodes that were etched too long, photooxidized, or not pretreated in oxygen-containing solution do not give straight Mott/Schottky plots (Figure 5a). The flat-band potential obtained from extrapolating a straight line through the curved plot to $1/C^2 = 0$ therefore is dependent on the potential range chosen for linearization and becomes arbitrary. Measurements with different ac frequencies show a strong dispersion mainly changing the slope of the Mott/Schottky plot.

This behavior changes dramatically after the cathodic pretreatment of the electrode described above, as shown in Figure 5b. The Mott/Schottky plot is straight even over a 10 -V potential range for sufficiently fast measurements (about 0.5 V/s) and is independent of frequency in the range 1 – 30 kHz. The reproducibility of the flat-band potential was within about 100 mV. Scanning the potential during the measurement at less than 0.5 V/s leads again to curved plots over a potential range of several volts, due to an increase of the capacity values within the time scale of the measurement. This shift is demonstrated in Figure 5b, which shows Mott/Schottky plots obtained by scanning the potential in opposite directions after prepolarizing the electrode at -1.1 and $+6$ V(SCE), respectively. The capacity values after anodic prepolarization are higher, leading to a parallel displacement of the Mott/Schottky plot, which nevertheless remains straight. The amount of the capacity shift occurring between anodic and cathodic sweep depends on the time between the scans and on the quality of the electrode, i.e., the size of the dark currents. The shift of the values upon prepolarizing the electrode at positive potentials in the dark is reversed immediately if the electrode potential is brought back to potentials where cathodic currents start to flow (cathodic potential of -0.6 V(SCE)).

The average flat-band potential determined for the CdS (0001) Cd surface of different electrodes is -1.75 ± 0.15 V(SCE). The uncertainty in determining the flat-band potential is mainly due

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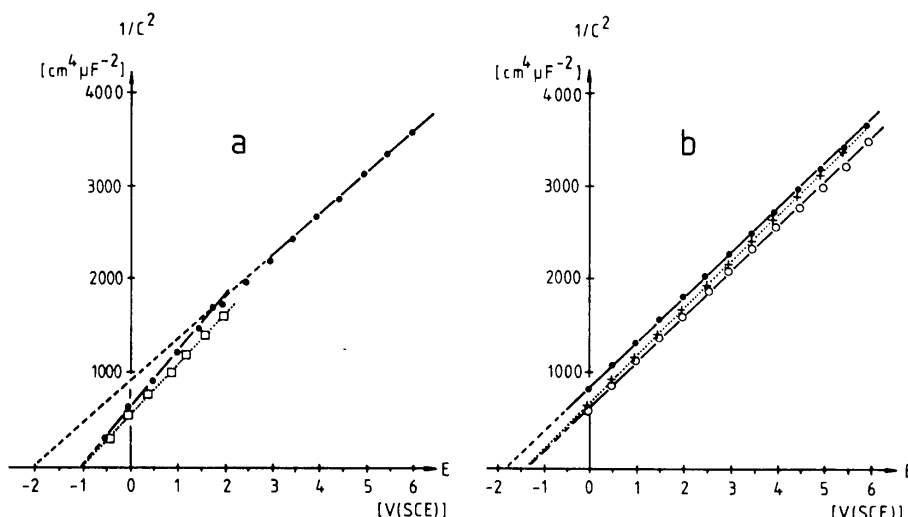


Figure 5. Mott/Schottky plots obtained from an CdS-(0001) Cd (a) polished and etched as usual (30 s with concentrated HCl), taken (●) with a scan rate of 0.5 V/s and (□) quasistationary, (b) polished, etched for 5 s in 20% HCl and prepolarized at -1.1 V(SCE) in oxygen-saturated 0.1 M K₂SO₄ solution, (●) anodic and (+) cathodic scan (0.5 V/s) after cathodic prepolarization, and (○) cathodic scan after anodic prepolarization (5 min at +6 V(SCE)).

to the fact that the $1/C^2$ plot has to be extrapolated over more than 1 V. The reason for this rather large extrapolation range is that the assumed simple equivalent circuit of a capacitance in series with a resistance is not valid anymore, if potential-dependent dc dark currents start to flow (compare Figure 3a).

Measurements with use of the (0001) S surfaces after identical pretreatment conditions given considerably more anodic values ($E_{fb} \approx -0.9$ V(SCE)). This cannot be changed by prepolarizing the electrode at cathodic potentials in the presence of oxygen but was changed by adding H₂O₂ to the solution. Capacity measurements with CdS (0001) S electrodes prepolarized in the presence of H₂O₂ gave Mott/Schottky plots very similar to those obtained from the CdS (0001) Cd surface, i.e., they intercepted the potential axis at a flat-band potential around -1.75 V(SCE).

Illumination shifts the Mott/Schottky plot in the anodic direction. This shift is only partially reversible. After the light is switched off, a considerable shift of a few hundred millivolts remains, the exact amount of which depends on the anodic corrosion current passed through the electrode. With this taken into account, a fast reversible parallel displacement of the Mott/Schottky plot by about 0.4–0.6 V remains, reflecting an anodic shift of the flat-band potential during illumination. Because of the irreversibility of a main part of the total shift due to photocorrosion, an intensity dependence was not studied.

Depositing RuO₂ on the surface leads to an onset of the hydrogen-evolution reaction already at about -0.9 V(SCE), eliminating the possibility of prepolarizing the electrode at -1.1 V(SCE). Impedance measurements performed with these electrodes after prepolarizing them at about -0.8 V(SCE), a potential where oxygen is reduced at these electrodes but probably only on the catalyst islands, lead to flat-band potentials around -1 V(SCE). Whether this is due to the lack of sufficient prepolarization or to a true shift of the flat-band potential has not been resolved.

In some cases very high capacity values have been obtained, leading to Mott/Schottky plots intercepting the potential axis at points as negative as -15 V(SCE). It has been found that these results were due to the polishing procedure applied. Aluminum holders were used for holding the electrode in place on the polishing apparatus. If by accident these holders were polished together with the CdS, aluminum particles could get rubbed into the electrode surface via the polishing cloth. The strange capacity values were reproducible by purposely doing this. Very high capacity values and nonsensical negative flat-band potentials were obtained also with electrodes that had certainly not been in contact with aluminum but that had not been etched after polishing. More analogies between aluminum-contaminated and unetched electrodes were found under illumination as will be described.

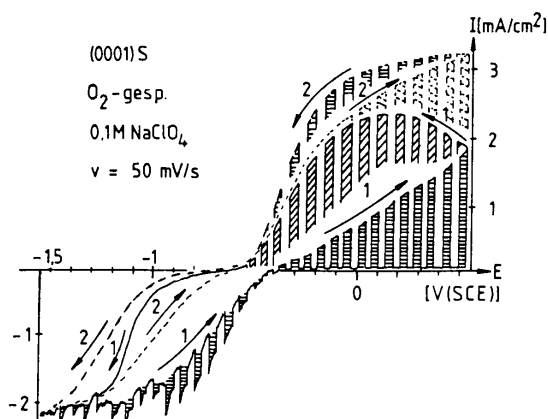


Figure 6. Current/potential behavior of unetched CdS under chopped illumination (compare text, numbers refer to first and second cycle; solution 0.1 M NaClO₄).

Photocurrent Behavior. Unetched CdS electrodes show a very peculiar behavior under illumination, as shown in Figure 6. Near the onset potential of reduction currents, cathodic photoeffects can be observed, and the anodic photocurrent rises only slowly at more anodic potentials. All the currents are strongly time dependent. Similar cathodic photoeffects with even stronger transients are seen with electrodes polished together with aluminum as described above (Figure 7).

Etching the electrode removes the cathodic photoeffects if no aluminum was rubbed into the surface. After prepolarization of these electrodes at -1.1 V(SCE) in the presence of oxygen, they exhibit photocurrent transients starting near the flat-band potential, i.e., at potentials where the reduction of oxygen or other suitable oxidized species is diffusion controlled. This will be discussed in the following paper in this issue.

Besides these photoeffects in the millisecond time scale, slower changes become visible in the photocurrent/potential dependence. Figure 8 shows a current/potential curve recorded by sweeping the potential of the electrode with 50 mV/s under intermittent illumination. The photocurrent becomes zero at about -0.6 V(SCE), i.e., just before the cathodic dark current occurs, by starting at rather anodic potentials and scanning in the cathodic direction. Several reduction peaks are seen until suddenly the photoeffect reappears again at about -1.2 V(SCE) (encircled region). The photocurrent starts at about -1.4 V(SCE) by sweeping back from the cathodic side. This behavior does not reflect a real potential

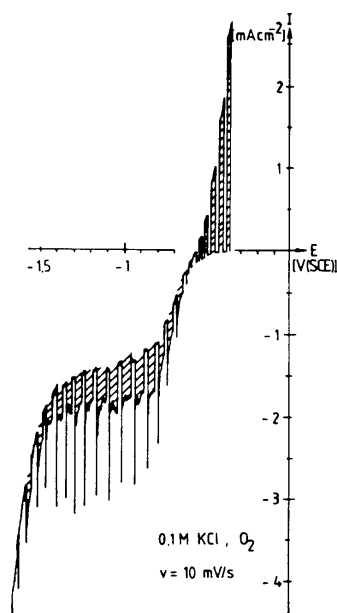


Figure 7. Current/potential curve from aluminum-contaminated CdS after etching (10 s in 20% HCl) obtained in oxygen-saturated 0.1 M KCl solution.

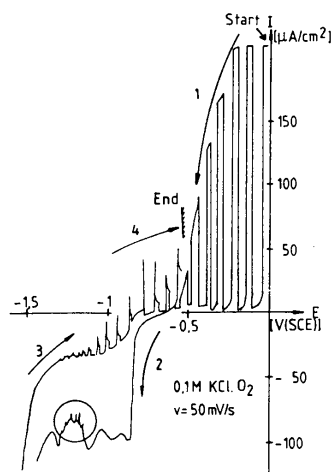


Figure 8. Current/potential behavior of etched CdS under chopped illumination as obtained in a first potential scan starting at 0 V(SCE) (encircled: reappearance of photoeffects not seen between -0.7 and -1.2 V(SCE)).

dependence of the currents but is due to the fact that the potential axis in this experiment displays also a time scale (as was proven by varying the scan rate). As will be discussed, the decrease of photocurrent at relatively anodic potentials is due to the change of the flat-band potential by photocorrosion, which can at least partially be reversed by passing reduction currents through the electrode in the presence of oxygen, shifting the flat-band potential back in the cathodic direction and by this bringing back the photoresponse at more cathodic potentials.

Discussion

The photoelectrochemical processes that we investigated turned out to be very complex. However, on the basis of results presented here and those published earlier by others and ourselves it is now possible to derive a consistent reaction scheme, as will be shown.

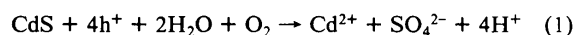
Photocorrosion and Cleaning of CdS. Two types of experiments have to be taken into account to understand the photoelectrochemical processes occurring on the surface of cadmium sulfide: experiments performed with illuminated CdS particles either in the form of suspensions or as colloids and photoelectrochemical experiments using CdS electrodes. The latter experiments have

the advantages that anodic and cathodic processes can be easily discriminated and that differences are seen between experiments performed in the dark and those under illumination. In addition the electrode potential can be changed deliberately. Experiments with illuminated particles are naturally limited to the potential where anodic and cathodic half-reactions occur equally fast. However, their advantages are that they are easy to perform and that a suspension provides a large illuminated area and therefore a high yield of reaction products. These products now should simply be the result of combined anodic and cathodic partial reactions.

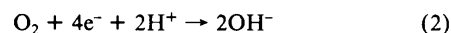
Illuminating CdS powders in moist air, Richardson found as early as 1886 that CdS "water colors" exposed to sunlight on "Whatman's best drawing paper" fade by oxidation to CdSO₄.¹³ This result and a few other hints¹⁴ that sulfate might be a photooxidation product of CdS have not been recognized by photoelectrochemists (compare, e.g., ref 15).

Later it was found that oxygen is reduced in CdS suspensions to give hydrogen peroxide, a reaction being crucially influenced by pollutants, electron donors, or catalysts in the solution.¹⁶ These experiments using CdS particles suspended in water were further investigated by Darwent^{17a} and later by Grätzel and co-workers.^{17b} They proved that oxygen uptake and hydrogen production are not simply competing reactions. However, a model for this observation was not provided.

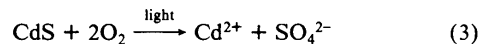
On the basis of our photoelectrochemical experiments with CdS single-crystal electrodes as reported here and in ref 7, the latter results can be easily understood as follows: Oxygen participates not only in the reduction but also in the oxidation process. Reducing oxygen at clean CdS electrodes leads only to OH⁻, and no peroxide can be found in the CdS⁻ cathode compartment after electrolysis. Sulfate is found as the main photooxidation product of CdS in the presence of oxygen under anodic polarization⁷ following the stoichiometry



where h^+ designates a hole. In connection with the cathodic reaction

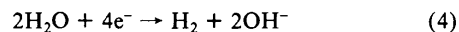


this leads to an overall stoichiometry for the photoprocess at illuminated CdS particles being given by

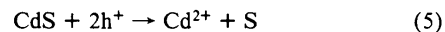


as we have reported.^{5c}

However, for an understanding of the results obtained with catalyst-loaded CdS particles suspended in water, three additional reactions have to be taken into account: the cathodic hydrogen evolution at metal-covered (RuO₂ or Pt) CdS



and the well-known anodic photocorrosion reaction of CdS in the absence of oxygen¹⁸



(13) Richardson, A. *Chem. News* **1886**, 54, 297.

(14) (a) Lal, P.; Ganguly, P. B. *J. Ind. Chem. Soc.* **1929**, 6, 547. (b) Babkin, M. P. *Z. Anal. Chem.* **1939**, 2, 118. (c) Montignie, E. *Bull. Soc. Chim. Fr.* **1939**, 6, 1191. Weber, E.-H. *Phys. Status Solidi* **1969**, 36, 175 and *Phys. Status Solidi A* **1970**, 1, 665.

(15) Gerischer, H. *J. Electrochem. Soc.* **1966**, 113, 1174.

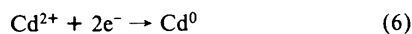
(16) (a) Stephens, R.; Ke, B.; Trivich, D. *J. Phys. Chem.* **1955**, 59, 966. (b) Pamfilov, A. V.; Mazurkewicz, Ya. S. *Khim. Zh.* **1962**, 28, 1014. (c) Harbour, J. R.; Hair, M. L. *J. Phys. Chem.* **1977**, 81, 1791; **1978**, 82, 1379. Harbour, J. R.; Wolkow, R.; Hair, M. L. *J. Phys. Chem.* **1981**, 85, 4026.

(17) (a) Darwent, J. R. *J. Chem. Soc., Phys. Commun.* **1981**, 145; *J. Chem. Soc., Faraday Trans. 2* **1981**, 77, 1703. (b) Grätzel, M. *Pure Appl. Chem.* **1982**, 54, 2369.

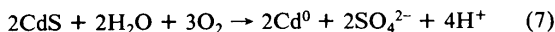
(18) (a) Williams, R. *J. Chem. Phys.* **1960**, 32, 1505. (b) Tyagai, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 9, 1419. (c) Roth, Ch. Ph.D. Thesis, Technische Universität München, 1966. (d) Fujishima, A.; Sugiyama, E.; Honda, K. *Bull. Chem. Soc. Jpn.* **1971**, 44, 304. (e) Inoue, T.; Watanabe, T.; Fujishima, A.; Honda, K. *J. Electrochem. Soc.* **1977**, 124, 719.

Therefore, during the illumination of catalyst-loaded CdS suspensions in oxygen-containing solutions, hydrogen is evolved and oxygen is consumed.

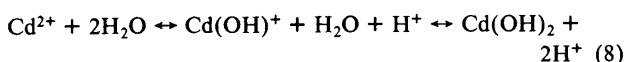
With increasing time of corrosion and with this increasing concentration of Cd^{2+} the cathodic reaction



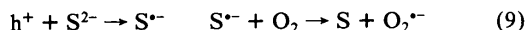
becomes more important. As can be seen from current/potential curves (Figure 2), dissolved Cd^{2+} is preferentially reduced at CdS. In connection with the anodic photocorrosion reaction in the presence of oxygen (eq 6) this should finally lead to an overall stoichiometry of



This overall reaction now explains the pH decrease we found with suspensions starting from neutral solution (ref 5b, compare also with ref 19), which only in the initial stage is caused by the complexing equilibrium of liberated Cd^{2+} :

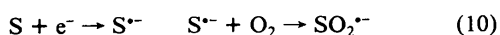


As a mechanism for the photooxidation reaction of CdS in the presence of oxygen Henglein had assumed that peroxide may be the main oxidation product.²⁰ Illuminating CdS colloids, he found small amounts of sulfate in the solution but attributed them at first to further oxidation of the corrosion product sulfur by $\text{O}_2^{\cdot-}$ or H_2O_2 in a following side reaction, though he modified this in later papers.²¹ Henglein took up Gerischer's idea of a radical ion being the first step in every photocorrosion process²² (compare also ref 23) and formulated as initial steps of the corrosion process



assuming that $\text{S}^{\cdot-}$ is further oxidized by oxygen. ESR spectra obtained from CdS powders heated in air²⁴ and irradiated in water^{16c} indeed show the formation of $\text{O}_2^{\cdot-}$. The ESR signal of the $\text{S}^{\cdot-}$ radical has been directly observed during band-gap irradiation of ZnS.²⁵

This intermediate may even have been formed by *reducing* previously formed S^0 on the surface of CdS, which then leads to the *oxidation* of sulfur (as we have proven by photoelectron spectroscopy^{7c}) probably via



The current/voltage curves in Figure 1 obtained after photo-oxidizing the CdS electrode (insert) actually show additional reduction peaks assumed to be due to this reaction.

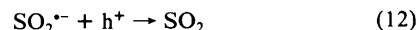
For the photoanodic oxygen uptake we proposed an analogous reaction:



following the formation of the surface radical $\text{S}^{\cdot-}$ to be the first

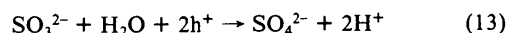
step.^{7c,8} In a very recent paper Meisel and co-workers²⁶ report the direct observation of sulfhydryl radicals produced by excitation of CdS and their efficient further reaction with oxygen to give the adduct radical $\text{SO}_2^{\cdot-}/\text{HSO}_2^{\cdot}$. After dimerization of the sulfhydryl radical, $\text{O}_2^{\cdot-}$ is formed, which produces H_2O_2 and sulfhydryl radicals, thus initiating a chain reaction. Accordingly, the formation of peroxide really seems to be a process initiated by the photooxidation product $\text{S}^{\cdot-}$ as formulated by Henglein. It explains why we were unable to detect peroxide formed at the CdS cathode. Interestingly enough, this means that the *reduction of oxygen* occurs via a *photoelectrochemical oxidation* process.

Further oxidation of the $\text{SO}_2^{\cdot-}$ then should lead to $\text{SO}_2/\text{H}_2\text{SO}_3$ formation according to

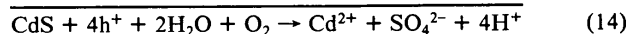
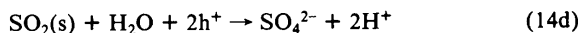
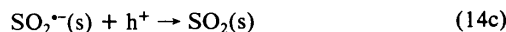
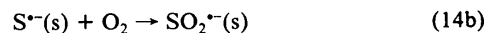
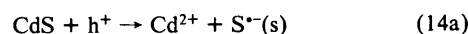


and we were indeed able to find traces of sulfite by careful ion chromatographic analysis of electrolytes in which CdS electrodes had been photooxidized in the presence of oxygen.²⁷

The oxidation of sulfite to give sulfate at CdS suspensions



has been studied by various authors. However, whether this reaction is a two-electron reaction as proposed by Matsumura et al.³¹ and by Bühler et al.³¹ or a one-electron reaction via $\text{SO}_3^{\cdot-}$ as shown by Gutierrez and Henglein²⁸ remains unclear. In our photocorrosion experiments using CdS electrodes²⁷ though, no dithionate was found, the usual coproduct of the sulfite oxidation by CdS. Either this may indicate a difference of the photocorrosion reaction compared to the oxidation of dissolved sulfite, or it may be due to a difference between our potentiostatically controlled experiments as opposed to the experiments using catalyst-loaded CdS particles. We therefore remain with the overall reaction scheme shown in eq 14 in which s indicates surface-bound species.



Improved Electrode Behavior. The further oxidation of initially formed sulfur on the surface of CdS by passing reduction current through the electrode in the presence of oxygen (prepolarization at -1.1 V(SCE)) made it possible probably for the first time to get really sulfur-free CdS surface, as demonstrated in ref 7c. We attribute the greatly improved electrode behavior to this fact. Our electrodes show not only very low anodic dark currents and very well defined reduction steps in the presence of appropriate redox couples but also no frequency dispersion in capacity measurements.

Current/potential curves from use of electrodes without this prepolarization procedure behave exactly like prepolarized electrodes after photooxidation, proving the fact that the surface is sulfur-covered already on freshly etched electrodes. This has been confirmed by Auger and XPS measurements.^{7c} However, current/potential curves of unetched samples as shown in Figure 6 behave even worse. Interestingly, they improve with time, as the comparison between the first and the second scan in Figure 6 reveals. The cathodic photoeffects disappear, and the photocurrent rises more steeply. Comparing the cathodic effects of unetched samples with those of electrodes polished together with aluminum (Figure 7) leads us to the assumption that both are based on the same effect: the charging of metal particles in the surface.

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(22) (a) Gerischer, H.; Mindt, W. *Electrochim. Acta* 1968, 13, 1329. (b) Gerischer, H. *Surf. Sci.* 1969, 18, 97. (c) Gerischer, H. *Faraday Spec. Discuss. Chem. Soc.* 1980, 70, 137.

(23) (a) Frese, K. W.; Madou, M. J.; Morrison, S. R. *J. Phys. Chem.* 1980, 84, 3172. (b) Nakato, Y.; Tsumura, A.; Tsubomura, H. *Chem. Lett.* 1981, 127, 383.

(24) (a) Sootha, G. D.; Padam, G. K.; Gupta, S. K. *Phys. Status Solidi A* 1979, 52, 125; 1980, 58, 615. (b) Padam, G. K.; Singh, B.; Gupta, S. K.; Sootha, G. D. *Phys. Status Solidi A* 1982, 71, 169.

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It has been reported several times that etching of the surface improves the electrode behavior of CdS.²⁹ This was attributed to the removal of "imperfections", "doping atoms", "surface defects", or "surface states", which act as electron traps and lead to high surface recombination, strong phototransients, and cathodic photoeffects. With the exception of donor atoms, no chemical explanation of these states has been given. It has been concluded from luminescence measurements though that "normal" surface states cannot be responsible for the effects at damaged surfaces.³⁰ For CdSe Tenne and Giritat proposed that a selenium layer causing a strong shift of the flat-band potential may be the reason for their cathodic photoeffects, because it might lead to an accumulation layer at potentials cathodic of the new flat-band potential.³¹

Our assumption that cadmium metal clusters are formed (together with sulfur) during polishing procedures or other mechanical damaging is in accordance with the results reported in these papers. It also provides an explanation for the experimental result that metal deposition³² and hydrogen formation³³ on semiconductor surfaces preferably occur on damaged sites. The metal clusters react exactly the same way as other metal "catalysts", i.e., they change the microscopic distribution³⁴ or form new surface states, providing charge transfer.³⁵ Furthermore, the dissolution of metal clusters explains much better the size of holes formed by etching the surface as reported by Tenne and Hodes²⁹ⁱ than does the dissolution of doping atoms.

It has been proven by photoelectron spectroscopy that sulfur covers the CdS surface even after very careful polishing and etching.^{7c} This is in accordance with results obtained from reflection measurements.³⁶ It is completely removed only by cathodic prepolarization. The reduction of the surface sulfur in the presence of oxygen as seen in I/E curves can actually be shown to result in the oxidation of sulfur. Sulfur(0), which is reduced to S^{2-} in a cathodic process (eq 10), is finally oxidized in the presence of oxygen to give sulfur(IV) or sulfur(VI). Assuming the formation of the same intermediate that is involved in the photooxidation process, we therefore proposed the reaction sequence 14a and 14b, which after further oxidation either by holes from CdS or by oxygen finally leads either to sulfite (eq 14c) or to sulfate (eq 14d). This reaction sequence should probably be valid also for CdSe, for which "cathodic stripping" has been shown to improve the electrode behavior.³¹ However, it remains to be investigated whether oxygen plays the crucial role in this process also, as it does for CdS. For CdTe, cathodic cleaning from Te occurs also in the absence of oxygen.³⁷

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TABLE I: Flat-Band Potential of CdS (Literature Values)

E_{fb} V(SCE)	electrolyte	remarks ^a	ref 35	
-0.74	pH 13	S, MS	Haberkorn	a 1967
-0.74		S, MS	Tyagai et al.	b 1971
-0.77	pH 4.8	S, MS	Gomes et al.	c 1977
-0.99	pH 9.2	S, MS	Gomes et al.	c 1977
-0.90	1 M NaOH	S, MS	Ellis et al.	d 1977
-0.85	acidic, Cd ²⁺	S, MS	Minoura et al.	e 1977
-0.83		I_{ph}^2	Ginley et al.	f 1978
-0.8		S, MS	Gobrecht et al.	g 1979
-1.28		S, MS	Gissler et al.	h 1982
-0.91	pH 6–10	P, MS	Dewitt et al.	i 1983
-1.45	cystein	P, MS	Dewitt et al.	i 1983
-0.2		S, I_{ph}	Kobayashi et al.	ref 1983
-0.4	pH 6.8	P, I_{ph}	Jackowska et al.	j 1983
-0.73	neutral	S, MS	Reeves et al.	k 1984
-0.74	pH 2	S, MS	Bruzzoni et al.	l 1984
-0.59	pH 3.5	S, MS	Hodes	m 1984
-0.62	pH 12.0	S, MS	Hodes	m 1984
-0.4 to -0.3	pH 4	S (S side), MS	Pentovelis et al.	n 1986
-0.6 to -0.7	pH 4	S (Cd side), MS	Pentovelis et al.	n 1986
-0.9	pH 0–14	S, MS	Nathan et al.	o 1986
-1.42	pH 0–14, cysteamine polysulfide	S, MS	Nathan et al.	o 1986
-0.87	pH 2–13, S ²⁻	S, MS	Watanabe et al.	p 1974
-1.39	pH 2–13, S ²⁻	S, MS	Watanabe et al.	p 1974
-1.25	polysulfide	S, MS	Ellis et al.	d 1977
-1.10	alkaline, S ²⁻	S, MS	Minoura et al.	e 1977
-1.2	polysulfide	S, MS	Richardson et al.	q 1981
-0.67	pH 8–12, S ²⁻	P, I_{ph}	Jackowska et al.	j 1983
-1.05	polysulfide	P, MS	Murthy et al.	r 1984
-1.3	pH 13, S ²⁻	S, P, MS, I_{ph}	Finlayson et al.	s 1985
-1.3	pH 4, S ²⁻	S, MS	Pentovelis et al.	n 1986

^aS = single crystalline, P = polycrystalline electrode; determined by MS = Mott/Schottky plot, I_{ph} = photocurrent onset, I_{ph}^2 = photocurrent squared.

Flatband Potential. As seen in Table I very different values for the flat-band potential of cadmium sulfide can be found in the literature.³⁸ This depends only partially on the differing methods and electrode types used. In a recent paper by Reeves and Cocivera^{38k} it was shown how sensitive capacity measurements are to sulfur on the surface. This is true for the slope and intercept of the Mott/Schottky plot as well as for the frequency dispersion found in most of the other investigations (compare e.g. ref 39). Using freshly polished and etched electrodes, Reeves and Cocivera see no frequency dependence and assume this to be the most accurate value. They also see a cathodic shift of the flat-band potential after cathodic prepolarization, but they attribute this to adsorbed sulfide formed by the reduction of sulfur.

On the basis of our results obtained from electrochemical measurements and more directly from surface spectroscopy (Auger

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(39) Dutoit, E. C.; Van Meirhaeghe, R. L.; Cardon, F.; Gomes, W. P. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 1206.

and XPS),^{7c} we know that the only way to get a sulfur-free CdS surface is by cathodic prepolarization in the presence of oxygen. On the other hand, there are charging processes in the millisecond time scale influencing the capacity measurements. They can be seen either in potential step or in photocurrent transient measurements (compare the following paper in this issue). This means that the actual values of the flat-band potential derived from Mott/Schottky measurements depend strongly on the charging condition of the surface. Defining the flat-band potential as the potential at which the bands are flat means that electron density in the conduction band at the surface is equal to that in the bulk. At the clean (0001) Cd surface and possibly also at the (0001) S surface the flat-band potential occurs around -1.8 V(SCE), as obtained after cathodic prepolarization at potentials negative of about -0.8 V(SCE) in a fast potential scan. How fast the scan has to be depends mainly on the quality of the electrode, i.e., the anodic dark currents that change the surface charge. A scan rate of 0.5 V/s enabled us to get straight Mott/Schottky plots over 10 V, i.e., over an extremely large potential range.

Capacity measurements of the (0001) S surface following the same pretreatment as used for the (0001) Cd surface (prepolarization at about -1 V(SCE) in oxygen-saturated solution) result in Mott/Schottky plots displaced about 0.9 V in the anodic direction. However, prepolarizing the electrode at this potential in H_2O_2 -containing solution shifts the plot of about the same position as that of the (0001) Cd surface. Whether this is due to a destruction of the surface exposing more Cd atoms to the electrolyte or whether it is due to insufficient cleaning of the S surface from S^0 without the H_2O_2 remains unclear. Ultrahigh vacuum measurements of the adsorption of oxygen to CdS indicate strong differences in the surface energetics of the two opposite (0001) surfaces.⁴⁰ Both sides show also very different etching behavior.⁴¹ Electrochemical measurements in the presence of sulfide in the solution as described in ref 38e are indications pointing in the same direction, i.e., that the two surfaces behave differently.

The occurrence of a very negative flat-band potential for clean CdS surfaces is supported by measurements of photocurrent transients as reported in the following paper in this issue. Anodic photoeffects are detectable down to about -1.6 V(SCE). The cathodic shift of the band edges with removal of surface sulfur is clearly seen in the current/potential dependence under intermittent illumination (Figure 8). For instance, starting from anodic potentials, the photocurrent disappears at around -0.6 V(SCE) and occurs again at around -1.3 V(SCE) during the cathodic sweep, indicating the cathodic shift of the flat-band potential, which is in good agreement with the capacity measurements.

It is interesting to note that capacity measurements performed in the presence of sulfide in the electrolyte yielded the same Mott/Schottky plot as those obtained in sulfide-free solution after cathodic prepolarization in the presence of oxygen. On the other hand, after electrochemical experiments in sulfide solution strong illumination is needed to shift the capacity values to more anodic potentials. Anodic prepolarization in the dark does not change the Mott/Schottky plot as it does without sulfide. Even using freshly etched CdS electrodes leads to the more negative capacity data that are normally obtained only with "electrochemically cleaned" surfaces.

We therefore assume that the sulfide in the electrolyte has two effects: On one hand, it removes surface sulfur by complexation leading to a "chemical cleaning". Washing the electrode surface with sulfide solution and then thoroughly rinsing with sulfide-free water also lead to an improved electrode behavior. On the other hand, sulfide prevents the accumulation of anodic charges in the surface: in the presence of sulfide only very small phototransients

are seen, and light does not lead to the fast anodic shift of the capacity data seen in the absence of a redox couple.

These two effects are probably important for many thio compounds, some of which have been shown to shift the flat-band potential of CdS (compare the table and the survey given in ref 42). This interpretation contradicts the generally accepted model of the cathodic shift being due to adsorption of the negatively charged RS^- ⁴³ and especially the results of Minoura et al.,^{38c} who report that the shift of the flat-band potential is proportional to the S^{2-} concentration in the electrolyte. However, there are two major objections against their interpretation: on one hand, their electrodes had been etched in concentrated HCl, which leads to a thick yellow surface layer of sulfur visible by the naked eye. On the other hand Figure 2 in their paper does not necessarily prove their interpretation, especially when taking into account a value of -0.85 V(SCE) for the $[\text{S}^{2-}] = 0$ value. Their flat-band potentials seem to approach a value of -1.5 V(SCE) for the higher sulfide concentrations. Their result that sulfide shifts the flat-band potential of the Cd surface more than that of the S surface is in agreement with our interpretation.

Illumination of the electrode has exactly the opposite effect. There is an important irreversible shift of the capacity data by the photoanodic sulfur formation that occurs even in oxygen-flushed solution. In addition, there is the shift of the flat-band potential by positive charging of the surface states as we reported in 1980.⁴⁴ According to our new results, we estimate this shift to be between 300 and 600 mV in saturation. About the same shift is found in the dark after adding, e.g., Fe^{3+} to the solution.

Summary

Crucial for the reanalysis of the CdS photoelectrochemistry was the understanding of the CdS surface chemistry and of the central role of the surface state S^{\bullet} in both charge-transfer and corrosion processes. Its reductive formation from surface sulfur and further reaction with oxygen lead to an electrochemical cleaning of the surface. As a consequence, probably for the first time measurements of the clean CdS surface became possible. They show that the true flat-band potential of CdS-(0001) Cd is -1.8 V(SCE), about 1 V more negative than generally assumed. The opposite (0001) S surface may have a considerably more anodic flat-band potential of about -0.9 V(SCE), though definitive results on this were not yet obtained.

S^{\bullet} is believed to be also the first intermediate in the photo-oxidation of CdS leading to sulfur in the absence of oxygen and to sulfate in the presence of oxygen in the electrolyte. A detailed reaction mechanism for the photocorrosion is proposed based on experimental data in accordance with results reported in the literature. The strange electrode behavior of unetched CdS electrodes is understood on the basis of Cd clusters in the surface acting as charge traps. Their dissolution by acids leads to the improvement of the electrode behavior by etching. The other surface contaminant changing the electrode behavior, sulfur, can also be removed chemically by washing the electrode with sulfide solution.

In conclusion, the electrode behavior of CdS is strongly influenced by its surface chemistry. However, the results reported in this paper and their interpretation further support our experimental result that CdS is not able to split water. Therefore, the better understanding of this material seems to make it less attractive for application-oriented photoelectrochemistry.

Registry No. CdS, 1306-23-6; SO_4^{2-} , 14808-79-8; K_2SO_4 , 7778-80-5; NaClO_4 , 7601-89-0; RuO_2 , 12036-10-1; KCl, 7447-40-7; Cd, 7440-43-9; Pt, 7440-06-4; S, 7704-34-9; O_2 , 7782-44-7.

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