

Adsorbed Thiosulfate Intermediate of Cadmium Sulfide Aqueous Photocorrosion Detected and Characterized by in Situ Infrared Spectroscopy

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Received: February 5, 1998

In situ infrared spectroscopy has been used to show that aqueous cadmium sulfide photocorrosion leads to solution sulfate via an adsorbed thiosulfate intermediate. Infrared spectra were recorded from thin films of colloidal cadmium sulfide deposited on zinc selenide internal reflection elements and in contact with aqueous solutions. Infrared absorptions at 1005 and 1152 cm^{-1} have been ascribed to adsorbed thiosulfate by comparisons with the corresponding absorptions in solution. Simultaneous in situ photolysis and infrared spectroscopy showed that adsorbed thiosulfate was initially formed but gradually converted to sulfate. Adsorption isotherm data, derived from absorbances in the infrared spectra, showed that thiosulfate is strongly adsorbed and that sulfate is weakly adsorbed to cadmium sulfide. This accounts for the lack of detection of thiosulfate in solution when photocorrosion occurs.

Introduction

Cadmium sulfide is an important semiconductor because of its potential for efficient conversion of solar energy to electricity and for its photocatalytic activity.¹ However, CdS readily photocorrodes in aqueous media containing oxygen when exposed to visible light. It is generally recognized that the end sulfur product in solution of CdS photocorrosion in the presence of oxygen is the sulfate ion.^{2,3} However, despite many photoelectrochemical studies where surface molecular structure is important, details of the intermediate steps in the photooxidation of surface sulfide ions to solution sulfate have not been elucidated.

Solid/solution interfaces have posed greater experimental challenges than solid/gas interfaces. However, the details of structure and reactions at solid/solution interfaces have now begun to be revealed by in situ scanning tunneling and atomic force microscopies⁴ and in situ surface-enhanced Raman, infrared, and sum-difference spectroscopies.⁵ The recent development of in situ infrared spectroscopy of species adsorbed at hydrous oxide surfaces^{6,7} has suggested that infrared spectroscopic analysis of many solid/solution systems of natural and technological significance may now be carried out.

In this work we have applied in situ internal reflection infrared spectroscopic methods to analyze the surface chemical and photochemical behavior of cadmium sulfide colloidal films in contact with aqueous solutions. The infrared spectra have revealed that thiosulfate is a significant adsorbed intermediate in the photooxidation of the sulfide ion at the CdS surface, and this appears to be the first time this has been observed. Further studies of this system are in progress to determine the influence of adsorption of inert ligands and pH upon the photocorrosion process.

Experimental Section

Colloidal cadmium sulfide was prepared by slow addition at room temperature of 25 mL of aqueous 0.04 M cadmium nitrate

solution and 25 mL of 0.04 M aqueous sodium sulfide solution to 50 mL of water.⁸ These solutions and the water were purged with oxygen-free nitrogen before mixing, and only Milli-Q water was used. The CdS colloid, which was prepared under laboratory fluorescent lighting, was subsequently stored in the dark. Cadmium nitrate 4-hydrate (Reidel de Haën, für Analyse) and sodium sulfide 2-hydrate (Ajax) were used as received. Sodium hydroxide (Merck) and sodium thiosulfate 5-hydrate (BDH, AR) were used as received to prepare aqueous solutions that were purged with oxygen-free nitrogen before use.

An X-ray diffraction pattern of the dried colloid particles was closely similar to that recently reported⁹ for cubic CdS nanoparticles. The UV-vis absorption spectrum of the colloidal solution¹⁰ indicated an average particle size of 5 nm.

CdS colloidal films were deposited on a ZnSe 45° single internal reflection ATR prism (Harrick Scientific Corporation) by room-temperature evaporation in air of 100 μL of the 0.01 M CdS colloid solution. These films were stable to washing with aqueous solutions and were removed from the prism by polishing with aqueous alumina powder (0.015 μm) slurry on a polishing microcloth (Buehler), brief sonication in water, and rinsing with water.

Infrared spectra were recorded with a Digilab FTS60 spectrometer fitted with a DTGS detector and a Harrick prism liquid cell accessory. The optical bench was purged with dried air. Spectra of CdS films in contact with solutions were normally recorded with a hemispherical glass solution chamber¹² sealed to the ZnSe surface with an O-ring. For isotherm measurements, solutions of successively increasing concentration were flowed through the cell. Each spectrum was calculated from 64 scans at 4 cm^{-1} resolution.

Photolysis was conducted using a Pluraflex HL150 halogen light source rated at 150 W. The light was directed to the film via a 7 mm diameter fiber optic cable.

Results and Discussion

Cadmium sulfide is not expected to show any significant infrared absorptions above the lattice modes that are observed¹¹

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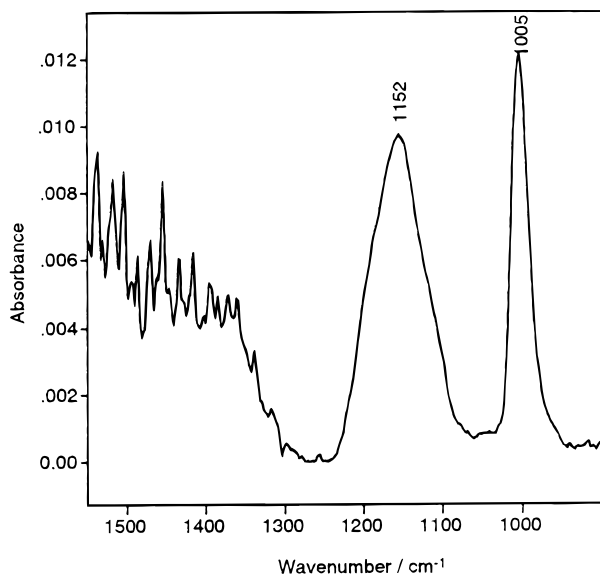


Figure 1. Internal reflection infrared spectrum of a CdS film deposited on a ZnSe prism by evaporation of 100 μ L of an aqueous 10^{-2} M CdS colloid solution.

in the 300–200 cm^{-1} region. However, the infrared spectrum of the CdS film deposited on the ZnSe prism as shown in Figure 1 has a number of absorptions in the 1550–900 cm^{-1} region. There is a sharp absorption at 1005 cm^{-1} and a broader absorption peak at 1152 cm^{-1} with a further broad absorption band above 1300 cm^{-1} . This CdS film was formed by overnight drying in air with minimal exposure to laboratory lighting, washed with water to remove the sodium nitrate, and dried in air before the spectrum was recorded.

We have established, with previous infrared studies of oxide surfaces,^{12,13} that adsorbing surface contaminants may be removed by washing with alkaline aqueous solutions. The spectrum shown in Figure 2a was recorded when the CdS film was washed with 0.01 M aqueous NaOH solution. For this spectrum the film was initially prepared by sol evaporation and washed thoroughly with water and the reference spectrum was recorded for the film in contact with water. The Figure 2a spectrum shows that the alkaline wash treatment has removed species, with prominent absorptions at 1005 and 1152 cm^{-1} as well as minor absorptions at ~ 1370 and ~ 1450 cm^{-1} , from the CdS surface. The absorbance losses of the 1005 and 1152 cm^{-1} bands are very similar to the absorbances of the corresponding bands in Figure 1. Thus the alkaline wash appears to remove almost all of the adsorbing species.

Figure 2c shows the infrared absorption spectrum of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution recorded with respect to water on a bare ZnSe prism. The absorptions at 995 cm^{-1} ($\nu_1(\text{a}_1)$) and 1114 cm^{-1} ($\nu_4(\text{e})$)¹² show a clear resemblance to some of the absorptions in Figure 2a and suggest that thiosulfate is the predominant species on the CdS surface. The CdS film, which had been treated with the 10^{-2} M NaOH wash, was then exposed to 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$ solution to test this tentative assignment. The resulting spectrum, relative to the spectrum of the alkali-washed film, is shown in Figure 2b. There is no detectable contribution to this spectrum from solution thiosulfate species at this concentration. This clearly confirms that the adsorbed species is thiosulfate.

The evidence in Figure 1 and Figure 2a, for thiosulfate adsorbed on aqueous CdS colloid particles exposed to visible light, indicates that photocorrosion is occurring under these conditions. Furthermore, the photooxidation of surface sulfide

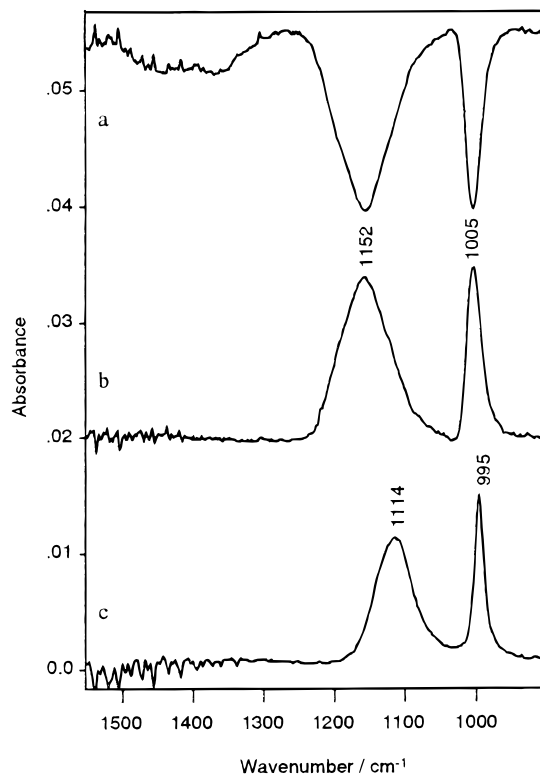


Figure 2. Internal reflection infrared spectra of (a) the CdS film in contact with 10^{-2} M NaOH solution, (b) the CdS film in contact with 10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$ solution, and (c) 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution.

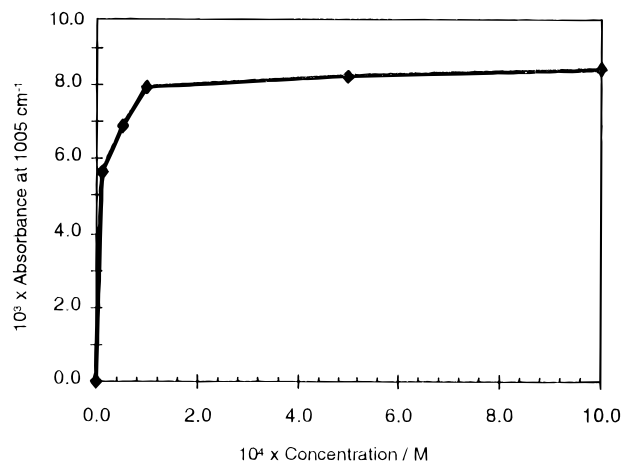


Figure 3. Adsorption isotherm from infrared absorbances at 1005 cm^{-1} for thiosulfate adsorbed to a CdS film from aqueous thiosulfate solutions containing 10^{-2} M NaCl.

ions results in a quite strongly bound adsorbed thiosulfate species as indicated by the relatively strong alkaline conditions required for desorption. We have used the infrared absorbances of surface thiosulfate at 1005 cm^{-1} to obtain the adsorption isotherm¹¹ for thiosulfate solutions in 10^{-2} M NaCl. This data is shown in Figure 3 and indicates that there is saturation of thiosulfate adsorption on CdS in contact with a 10^{-3} M aqueous thiosulfate solution. Thus the spectrum shown in Figure 2b corresponds to saturated coverage, which is likely to be a thiosulfate monolayer. A linear plot of c/A versus c , where c is the solution concentration and A is the absorbance, gave a Langmuir¹² binding constant of $(1.2 \pm 0.3) \times 10^5 \text{ M}^{-1}$. This high binding constant confirms the strength of thiosulfate adsorption to CdS.

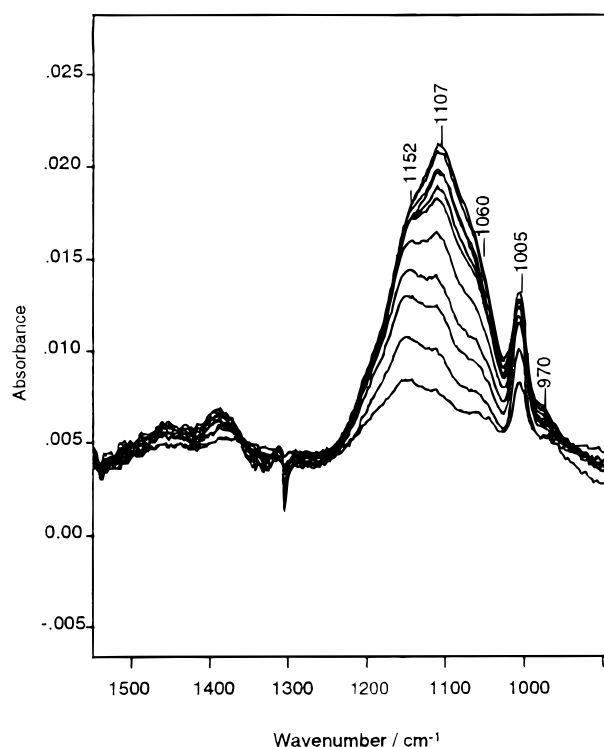


Figure 4. Time development of internal reflection infrared spectra of a CdS film under continuous visible photolysis and in contact with an oxygen-saturated 10^{-3} M HCl solution.

The significant difference between the spectrum of adsorbed thiosulfate and that of solution thiosulfate indicates that the adsorption is not merely due to surface charge but is chemical in nature. In general, if the binding of thiosulfate is via an oxygen the bands shift to lower wavenumber,¹³ but this is not observed here. Gabelica¹⁴ has correlated the vibrational spectra of monodentate and bridging thiosulfate in different coordination complexes. Absorptions of coordinated thiosulfate in the 1005–1012 and 1150–1170 cm^{-1} ranges are classified as arising from monodentate ligands. Thus the thiosulfate appears to have monodentate binding to a surface cadmium ion.

The time development of spectra arising from continuous in situ visible light photolysis of the CdS film in contact with 10^{-3} M oxygen-saturated aqueous HCl solution is shown in Figure 4. The CdS film for this experiment was prepared in the usual manner except that the alkaline wash was conducted in the absence of light. The HCl solution was continuously flowed through the cell at $1.1 \mu\text{L s}^{-1}$. The reference spectrum for the Figure 4 spectra was from the CdS film in contact with the HCl solution immediately prior to initiation of the photolysis.

The spectra in Figure 4 were recorded over 5 h at 30 min intervals except for the first four spectra, which were at 15 min intervals. The spectrum at 15 min indicates that thiosulfate is the predominant initial product of CdS photooxidation. However, there are additional absorptions at 1107, ~ 1060 , and $\sim 970 \text{ cm}^{-1}$, which become dominant at later times indicating the formation of another species. We have carried out in situ infrared spectroscopic adsorption experiments with sulfate solutions and have confirmed that these additional absorptions arise from adsorbed sulfate ion. Furthermore, adsorption isotherm measurements showed that sulfate was more weakly bound to CdS than thiosulfate with a Langmuir binding constant of $1 \times 10^3 \text{ M}^{-1}$.

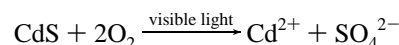
When the continuous in situ photolysis experiments were carried out under the same conditions as above but with

nitrogen-saturated solutions, the extent of photocorrosion to thiosulfate was much reduced and sulfate was not observed in the infrared spectra. Experiments carried out under the same conditions as above but in the absence of visible light gave no infrared spectral evidence for adsorbed thiosulfate or sulfate formation.

The minor absorptions at ~ 1370 and $\sim 1450 \text{ cm}^{-1}$ are due to adsorbed carbonate. While adsorbed carbonate can be removed by the alkaline wash treatment, as seen in Figure 2b, it is difficult to completely exclude carbon dioxide from these experiments. The sharp peaks above about 1400 cm^{-1} are due to incomplete subtraction of residual water vapor in the purge air. The very sharp peak at 1304 cm^{-1} is an instrumental artifact. With a band gap energy of 2.7 eV,¹⁵ ZnSe may contribute to visible light induced photoredox processes. The band edge energies of ZnSe relative to those for CdS¹⁶ favor photoreduction rather than photooxidation from any ZnSe \rightarrow CdS charge transfer arising from ZnSe absorptions. We therefore conclude that any ZnSe absorption of visible light does not significantly influence the CdS photooxidation.

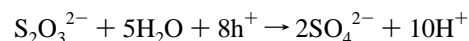
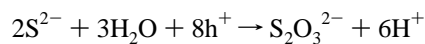
Conclusions

The results reported in this paper appear to be the first observation of thiosulfate as a significant adsorbed intermediate in the photocorrosion of CdS in aqueous solutions containing oxygen. From detection of Cd^{2+} and SO_4^{2-} in solution in previous work, the overall stoichiometry for the photoprocess is believed to be



In a detailed analysis of CdS photocorrosion experiments, Meissner et al.² have proposed that $\text{S}^{\bullet-}$, $\text{SO}_2^{\bullet-}$, and $\text{SO}_2/\text{SO}_3^-$ are intermediates of S^{2-} photooxidation to SO_4^{2-} at CdS surfaces in the presence of oxygen. Pelizzetti et al.¹⁷ have suggested the formation of thiosulfate at CdS surfaces by reaction of sulfite ion with atomic sulfur. Although sulfite ion adsorbs to CdS,¹⁸ there is no evidence for formation of adsorbed sulfite ion in the present photocorrosion study.

Rather, the photooxidation of sulfide ion at CdS surfaces appears to proceed via a strongly adsorbed thiosulfate intermediate to a weakly adsorbed sulfate ion in the following reactions:



The weakly bound sulfate ion is readily lost from the surface into solution. This accounts for sulfate having been the only significant sulfur species detected in solution when CdS photocorrosion occurs. The complexity of the above reactions makes it difficult to speculate at this stage on the detailed mechanisms of thiosulfate formation or its conversion to sulfate at the CdS surface.

The chemical state of a semiconductor surface is critical in determining the nature and kinetics of its interfacial reactions. The present work raises questions about the influence any adsorbed thiosulfate may have had on the variability of results in CdS photocatalysis experiments. In general, this paper indicates the importance of direct experimental observations of adsorbed intermediate species in solid/solution interfacial chemistry. The internal reflection in situ infrared spectroscopic methods used in this paper have considerable potential in this field.

Acknowledgment. This research was supported by the Research Committee and the Division of Sciences of the University of Otago.

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