

Surface analysis of semiconductor-incorporated polymer systems. 1. Nafion and cadmium sulfide-Nafion

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of nonadiabatic coupling matrix elements from SA-MCSCF/CI wave functions will be employed to study the nonadiabatic coupling between these two adiabatic states. Such an analysis is also relevant in assessing the role of this avoided crossing in the collisional dissociation process studied by CB. In this case, however, some idea of the state of CO⁺ "initially prepared" is required for a complete analysis of this problem.¹⁹

HS assigned to fifth vibrational progression observed in the photoelectron spectrum³ to the 3²Σ⁺ state. Increased credence can be given to this assignment in light of the considerably improved agreement in the *T_e* evinced in Table III. The decrease in ω_e and the increased well depth provided by the FOCI treatment also favor this assignment. It should be noted that the 3²Σ⁺ state determined at the MCSCF level differs qualitatively from the FOCI result. The results of HS appear to be (perhaps surprisingly) in better accord with FOCI PEC's.

In a recent study of NO⁺ Saxon et al.¹⁷ considered the possibility of valence-Rydberg mixing and concluded it was unimportant for (at least) the 1, 2³Π states. The good agreement between the

present ab initio results and the photoelectron spectrum strongly indicates a similar situation obtains in this case. For the 2²Σ⁺ states this conclusion is further supported (although the present basis is inadequate for a definitive conclusion) by the lack of a tendency toward "Rydbergization" in the (optimized orbital) description of the 3²Σ⁺ state for small *R* (*R* = 2.132 au). The location of the CO⁺ Rydberg states (i.e., CO²⁺ plus one orbiting electron) will be considered in a subsequent study in which the structure of CO²⁺ will be considered explicitly.

In summary the SA-MCSCF/FOCI wave functions presented in this work support the assignment of the fourth and fifth vibrational progressions in the photoelectron spectrum of CO given by Honjou and Sasaki. The importance of an avoided crossing between the 2²Π and 3²Π states (treated in this work with a three-state averaging technique) for the collision-induced decomposition of CO²⁺ reported by Curtis and Boyd is suggested.

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Surface Analysis of Semiconductor-Incorporated Polymer Systems. 1. Nafion and CdS-Nafion

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Nafion and CdS-Nafion membranes were investigated by scanning electron microscopy and X-ray photoelectron spectroscopy. Depending on the preparation method, samples dominated by either cubic or hexagonal phases of CdS can be prepared. Samples dominated by the cubic form of CdS have very rough surfaces compared to those dominated by the hexagonal form. The S(2p) binding energies indicate that the surface of the hexagonal form is rich in sulfate ions, whereas the surface of the cubic form is dominated by the sulfide ions of CdS. A gray-blue deposit formed on the cubic CdS-Nafion surface under UV irradiation is identified as atomic sulfur.

1. Introduction

CdS is an interesting semiconductor and photocatalyst with a relatively narrow band gap energy (2.4 eV). Studies using colloidal or powder suspension CdS systems have been reported.¹⁻¹² An alternative approach involves polymer-supported CdS. For example, Meissner et al.¹³ have used membranes consisting of CdS particles (~40 μm) physically embedded in a polyurethane film

and have studied a number of photolysis processes. Kuczynski et al.¹⁴ prepared dispersed CdS in a Nafion(125) membrane and examined its photochemical and photophysical properties.

Such semiconductor/polymer systems are attractive for several reasons: (1) the photoactive system is held in place and so is useful in flow systems, (2) the CdS-Nafion system can be removed for more facile analysis of the reaction solution and regeneration of the semiconductor particles, and (3) the polymer matrix itself may play a role in the operation of the system, e.g., by its ion exchange properties, concentrating some solution reactants and rejecting others.

Recently, we reported the preparation of CdS-Nafion(117) films and showed that the resulting crystal form of CdS (α, hexagonal, or β, cubic) was determined by the method of preparation.^{15,16} In the presence of Pt (either chemically deposited throughout the membrane or sputter deposited) and Na₂S (sacrificial electron donor), photochemical H₂ formation was observed. The activity was substantially higher with β- than with α-CdS and was comparable to that of colloidal systems.

A better understanding of these CdS-Nafion systems and especially the effect of crystal phase on the catalysis was desired. We report here our results on the characterization of Nafion itself

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and CdS-loaded (α and β) Nafion membranes.

2. Experimental Section

Nafion (Du Pont 117, equiv wt 1100, 0.018 cm thick) membranes were used for all experiments. All Nafion films were cleaned by boiling in concentrated HNO_3 and washing with boiling distilled water. The films were stored in distilled water.

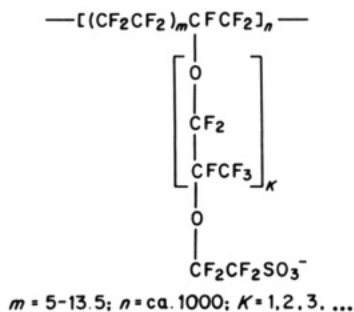
Films containing CdS (hexagonal and cubic) were prepared according to methods outlined in the previous paper.¹⁶ They were bright orange and opaque. The CdS crystal structures of these films were measured by X-ray powder diffraction (XRD). The crystal size was estimated as 200 Å from the XRD line widths. Scanning electron microscopy (SEM) was done with a JEOL JSM-35C system.

The films (Nafion and CdS-Nafion) were immersed in a Na_2S (0.1 M) solution with or without irradiation by a 1-kW xenon lamp. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Vacuum Generators ESCA Lab II system with Mg $K\alpha$ radiation (1253.6 eV). The core-level binding energies (BE) were all referenced to the surface hydrocarbon contamination C(1s) peak (284.5 eV). Before XPS measurements were taken, all films were dried in a desiccator overnight. The pressure in the spectrometer chamber was 3×10^{-8} torr during XPS observations.

Powders of CdS (99.999%, Aldrich), CdSO_4 (Mallinckrodt), and sulfur (sublimed, Fisher) were used as references.

3. Results

3.1. Nafion(117). The chemical structure of the Nafion film is given by the following formula:^{17,18}



XPS of the Nafion gives peaks for F(1s), C(1s), and O(1s) at BEs of 688.9, 291.3, and 531.9 eV, respectively (Figure 1). The F and C peaks are assigned to the $-\text{CF}_n-$ species, consistent with the report of Clark et al.¹⁹ It is more difficult to assign the O(1s) peak as there may be contributions from both the Nafion and contaminant adsorbed species. After a brief period of Ar^+ bombardment, the O(1s) peak broadened and its intensity decreased.

No sulfur peak from $-\text{SO}_3^-$ was observed with XPS either prior to or following Ar^+ bombardment. Previous studies of Nafion indicate that sulfonate ions and water molecules form cluster structures²⁰⁻²² that are distributed heterogeneously through the film.²³ No information exists, however, concerning the presence of sulfonate groups at the surface. The expected S(2p) peak intensity relative to that observed for F(1s) would have been detectable in our experiments on the basis of the overall S/F atomic ratio of Nafion and the XPS atomic sensitivity factors.²⁴ Thus, the results suggest that the surface concentration of sulfonate

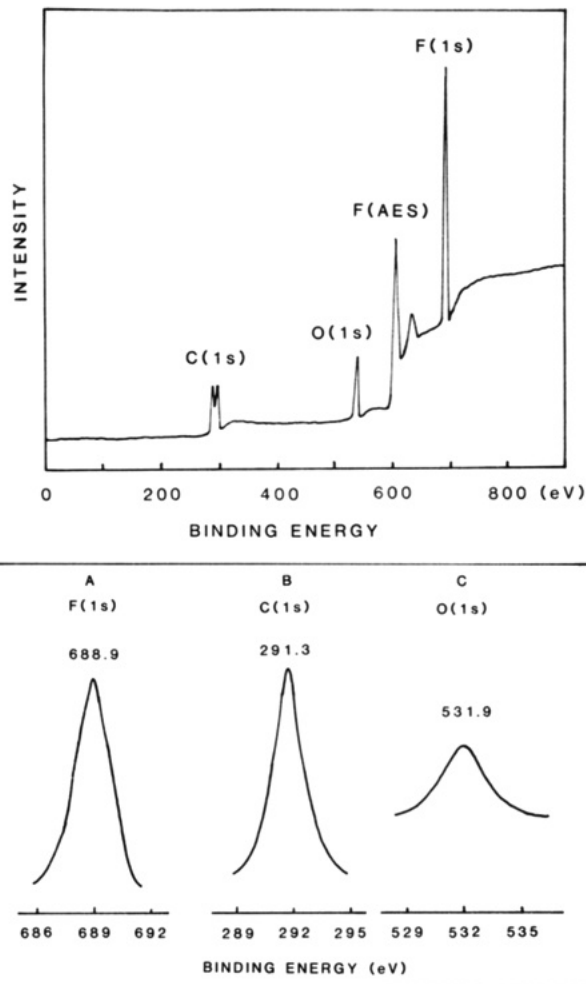


Figure 1. (a, Top) Broad-scan XPS spectrum of a Nafion film (Mg $K\alpha$ source). (b, Bottom) XPS spectra of Nafion films: (A) F(1s), (B) C(1s), (C) O(1s).

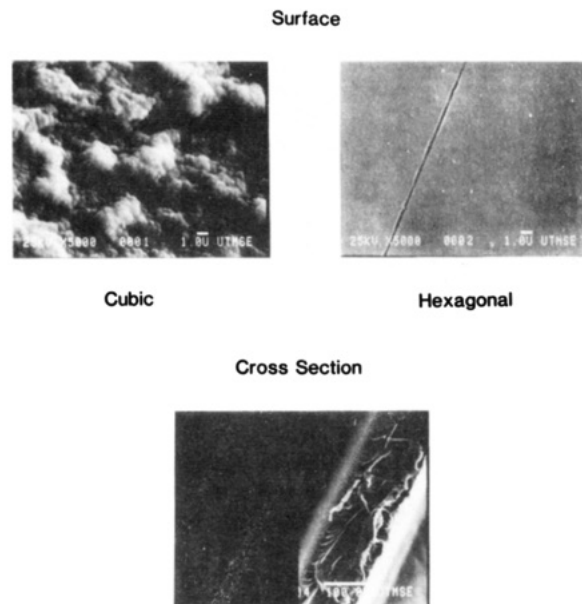


Figure 2. SEM photographs of hexagonal CdS/Nafion and cubic CdS/Nafion ($\times 5000$). The cross section is for a cubic CdS/Nafion film ($\times 200$). The left-hand side is the X-ray fluorescence from Cd.

is low relative to the bulk. This point is discussed below in conjunction with the formation of Cd compounds at the Nafion surfaces.

3.2. CdS-Nafion. Scanning electron microscopy (SEM) of the CdS films showed a striking difference in the surface roughness

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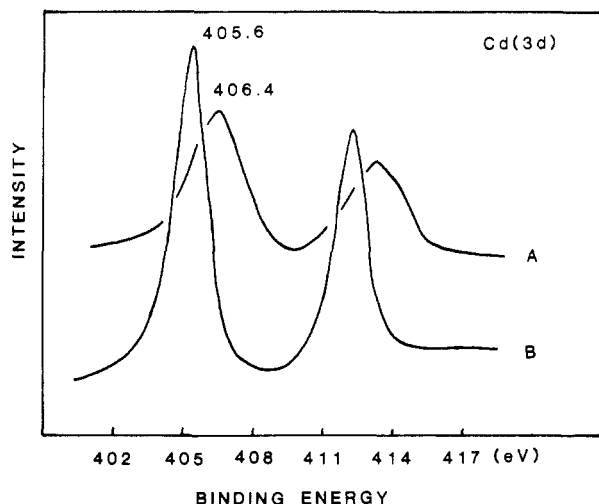


Figure 3. Cd(3d) XPS spectra of hexagonal CdS/Nafion (A) and cubic CdS/Nafion (B).

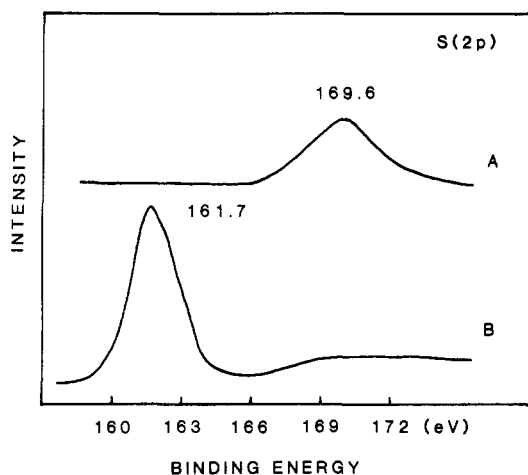


Figure 4. S(2p) XPS spectra of hexagonal CdS/Nafion (A) and cubic CdS/Nafion (B).

(Figure 2) of the cubic and hexagonal crystal forms. Large particles were observed for the cubic film, while the hexagonal film surface was flat and no particles were observed. Examination of a cross-sectioned film by SEM showed no distinguishable morphological differences between the two crystal forms in the interior of the Nafion. X-ray fluorescence analysis of Cd in the cross-sectioned films (Figure 2) showed that, in both, Cd was dispersed reasonably uniformly throughout the Nafion, with a slightly higher concentration near the outer surface.

The XPS of bulk reference samples were measured. The CdS and CdSO₄ powders both gave a Cd(3d_{5/2}) BE of 405.4 eV. With regard to the S(2p) region, CdSO₄ has a peak at 168.5 eV assigned to the sulfate ion, and CdS has peaks at 161.6 and 169.2 eV. We assign the former to the S²⁻ ion and the latter to a surface sulfate species. The results are in good agreement with others.^{25,26} Sublimed sulfur powder shows a peak at 163.3 eV.

The XPS results for both films are shown in Figure 3. The cubic CdS film (B) has a Cd(3d_{5/2}) BE of 405.6 eV, while the hexagonal CdS film (A) has a peak at 406.4 eV. After Ar⁺ bombardment of the hexagonal CdS film for a short time, the integrated Cd(3d_{5/2}) intensity increases. For the cubic CdS film, Ar⁺ bombardment left the Cd(3d_{5/2}) peak unchanged.

Figure 4 shows XPS for the S(2p) region. The cubic CdS film (B) has peaks at 161.7 and 168.9 eV. The higher BE disappears with Ar⁺ bombardment. The hexagonal film (A) has only one

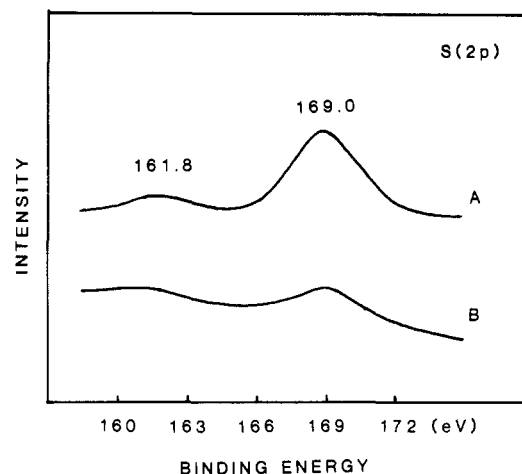
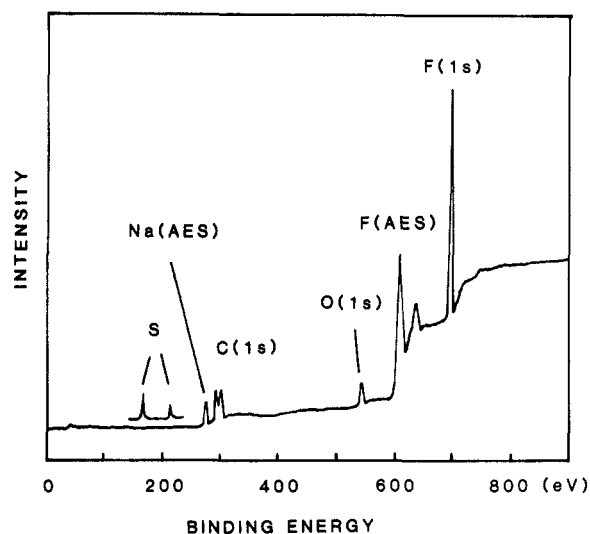


Figure 5. (a, Top) Broad-scan XPS spectrum of Nafion film soaked in Na₂S without irradiation. There was no detectable difference in a broad scan with irradiation. (b, Bottom) S(2p) XPS spectra of Nafion soaked in Na₂S without (A) and with (B) irradiation.

peak at 169.6 eV, which, after Ar⁺ bombardment, decreases in intensity and broadens. According to our results for the films and the reference materials, and after comparison with binding energies reported for cadmium and sulfur compounds,²⁷⁻³⁰ we assigned the Cd(3d_{5/2}) 405.6-eV peak to the Cd²⁺ ion of either CdS or CdSO₄ and the S(2p) 161.7-eV peak to the S²⁻ ion of CdS. The higher BE peaks [S(2p) 168.9, 169.6 eV] are assigned to surface sulfate species. The 406.4-eV BE for Cd in the hexagonal film is discussed below.

3.3. Na₂S Effect. As described in a previous paper,¹⁶ we used a Na₂S (0.1 M) solution as a sacrificial reagent when measuring the photochemical hydrogen formation. In this section, the effects of Na₂S on Nafion and cubic CdS-Nafion films with and without irradiation are shown.

3.3.a. Nafion 117. After soaking in a Na₂S solution (with or without irradiation) for three hours the films turned light grey. Figure 5 shows a broad scan XPS. Nafion and S(2p) peaks are observed. The BEs of C(1s) and F(1s) are similar to those of the fresh Nafion film.

As seen in Figure 5b, both the irradiated and unirradiated samples show S(2p) peaks at 161.8 and 169.0 eV, with the latter more intense. These are assigned to sulfide and sulfate species, respectively. After a 30-s Ar⁺ bombardment, both peaks disappear

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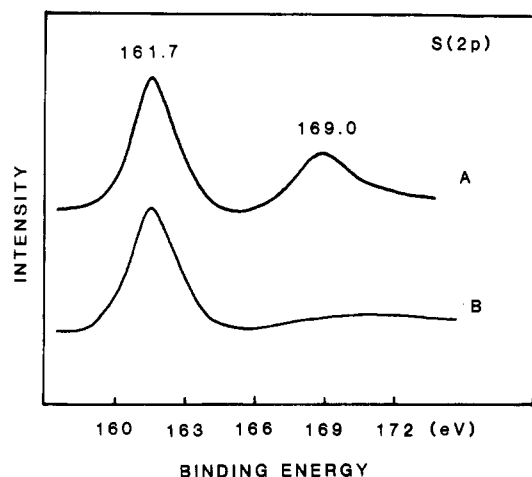


Figure 6. S(2p) spectra of cubic CdS/Nafion soaked in Na₂S without (A) and with (B) irradiation.

from both films, indicating they are concentrated on the Nafion surface. Apparently, some of the S²⁻ ions from the Na₂S are oxidized to the sulfate species, which may also be responsible for gray coloring. While the effect of sulfate ions on the photolysis process is not known, oxygen dissolved in the Na₂S solution does poison the photoproduction of hydrogen.

3.3.b. CdS-Nafion. The cubic CdS films were used for these experiments because of their high activity for hydrogen generation when platinized.¹⁶ Na₂S treatments were performed as in the pure Nafion experiments.

The cubic CdS films became covered by a gray-blue layer during irradiation, but the solution was clear and no precipitate was observed. This colored layer was removed by washing the film with boiling water. XPS of the irradiated film showed a spectrum indistinguishable from that of the fresh cubic CdS film. No new peak was observed due to the gray-blue deposit. Without irradiation, the gray-blue layer was not formed, and the S(2p) XPS had peaks at 161.7 and 169.0 eV (Figure 6). The 161.7-eV peak is assigned to the S²⁻ ion and the 169.0-eV peak to the surface sulfate species.

4. Discussion

Hexagonal CdS and cubic CdS films are strikingly different as revealed by both SEM and XPS measurements. We will concentrate this discussion on the XPS results.

Before washing, all of the films exposed to Na₂S are dominated in XPS by S(2p) associated with sulfide. After being washed for 1 h at 100 °C, the hexagonal CdS films show no S²⁻ ions in the XPS results and a Cd(3d_{5/2}) BE 1.0 eV higher than that of the cubic CdS film. Furthermore, the line width of the Cd(3d_{5/2}) peaks on hexagonal and cubic CdS films are 2.3 and 1.4 eV, respectively.

The Cd(3d) BE for the washed hexagonal film agrees very nicely with that measured for a Cd²⁺ ion-exchanged but unsulfided film (BE = 406.4 eV and line width = 2.4 eV). In the latter the Cd²⁺ ions are bound to cation exchange sites of Nafion. The relatively high BE is ascribed to a final state relaxation effect; cation exchange sites in Nafion are not very polarizable, so that core holes formed in Cd ions localized at these sites are not efficiently screened.

The surface atomic ratios (Cd/F, S/F, and C(Nafion)/F) calculated from the XPS peak areas are listed in Table I. The results indicate that the cubic CdS film has a higher surface concentration of Cd and S than the hexagonal film. It is interesting that the surface of the hexagonal film and the ion-exchanged Cd²⁺-Nafion film show similar Cd/F ratios. This, coupled with the high BE and broad line width for the Cd, suggests that the Cd is not present as sulfate. Rather, the sulfate may be associated with the Nafion leaving the Cd²⁺ in the same state observed prior to sulfiding. In passing, it is also noteworthy that the hexagonal films were subject to greater surface charging than the cubic films but about the same as for Nafion alone.

TABLE I: XPS Peak Ratios

ratio ^a	α-CdS (hexagonal)	β-CdS (cubic)	Cd ²⁺ - Nafion	Nafion
Cd(3d _{5/2})/F(1s)	0.04	8.40	0.06	
S(2p)/F(1s)	0.02 ^b	1.60		
C(1s)/F(1s)	0.10	0.10	0.10	0.10

^a Without relative atomic sensitivity adjustment. ^b Assigned to SO₄²⁻.

TABLE II: XPS Peak Ratios for CdS and Nafion Films Containing Cubic CdS

S(2p)/Cd(3d _{5/2})	CdS powder	cubic CdS-Nafion		
		un- treated	soaked in Na ₂ S	soaked and irradiated
low BE peak for S	0.18	0.19	0.25	0.25
high BE peak for S	0.05	0.02	0.12	0.02

From the Cd/F ratio for the Cd²⁺-Nafion system (Table I), an expected S(2p) XPS intensity can be calculated, assuming one Cd²⁺ is equivalent to two Nafion ion exchange sites. The expected sulfur intensity is a least a factor of 3 below our detection limits. This is consistent with the conclusion that the surface sulfonate concentration in Nafion is relatively low.

As indicated above, washing in boiling water changes the surface concentrations for the hexagonal but not the cubic samples. The data of Table I were taken after washing for 1 h. If instead the samples were washed for only 30 min, the Cd/F ratio was 0.12 for washing at 100 °C and 0.46 for washing at 25 °C. The Cd(3d_{5/2}) BE was at 405.4 eV, as observed for bulk cadmium sulfide and cadmium sulfate. This is consistent with the above picture and indicates that, for the hexagonal samples, the surface Cd is mobilized during washing and moves either into the film bulk or into solution. For the cubic case, washing in boiling water has no detectable effect on the XPS spectra, suggesting that the large CdS particles are not subject to this removal process.

Next, we explore the identity of the gray-blue layer (identified below as atomic sulfur) that develops on the cubic CdS film upon irradiation in the Na₂S solution. This deposit is not polysulfur since the S(2p) BE is 161.6 eV, which is not consistent with that for polysulfur (163.3 eV). Table II gives XPS-determined S/Cd ratios for several samples. This ratio for untreated (no Na₂S and no irradiation) cubic CdS is similar to that for powdered CdS, while the remaining samples show excess sulfur. That Na₂S exposure without irradiation does not produce this blue-gray layer suggests that it is also not due to S₂²⁻. When CdS or platinized CdS is irradiated in Na₂S, S₂²⁻ ions have been shown to form and the solution yellows.¹² We have found, however, that S₂²⁻ is unstable (the yellow color disappears) and is oxidized to SO₄²⁻ in the presence of oxygen. Thus, S₂²⁻ may also be eliminated as a candidate.

We now turn our attention to atomic sulfur. XPS results have been reported from S/Ni(100)³¹ and S/Ag(111)³² systems in which atomic sulfur was deposited on the crystal surfaces by decomposition of preadsorbed H₂S and electron-activated H₂S, respectively. The observed BEs for these atomic sulfur layers were 162.1 and 161.8 eV, respectively, both of which are close to our observed S(2p) BE and overlapping heavily with S²⁻. Thus we suggest that the gray-blue deposit is due to an atomic sulfur species, formed by the reactions



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In this model, reaction 3 is faster than reaction 4, if atomic sulfur accumulates. Atomic sulfur has not been found in colloidal or powder suspension systems containing a sacrificial electron donor, so that there seems to be a direct involvement of the host Nafion. Finally, since the S/Cd ratio for the irradiated cubic CdS sample approaches that for CdS powder after a short period of Ar⁺ bombardment, the atomic sulfur layer appears to be, at most, a few monolayers thick.

As indicated in Table II, the surface of the cubic CdS film soaked in Na₂S solution without irradiation is covered with excess S²⁻ ion of Na₂S. Surface sulfate species is also present. The data indicate that the S²⁻ ion of Na₂S or H₂S is strongly adsorbed on the CdS-Nafion surface and is oxidized to sulfate (Figures 4 and 6) without irradiation.

5. Conclusions

On the basis of the results reported here, we draw the following conclusions:

(1) The concentration of surface cation exchange sites in Nafion is small.

(2) The small CdS particles at the surface of the hexagonal CdS films are subject to dissolution in boiling water, whereas the large CdS particles at the surface of the cubic CdS films are stable in boiling water.

(3) After extensive washing, the surface of films containing cubic CdS remains dominated by sulfide ions of CdS, whereas the surface of films containing the hexagonal form are altered, leaving surface sulfate associated with the Nafion and Cd²⁺ associated with cation exchange sites.

(4) Adsorbed sulfide ions on Nafion and CdS-Nafion are oxidized to sulfate ions at 300 K in the presence of oxygen.

(5) The gray-blue deposit formed on cubic CdS-Nafion surfaces under irradiation is identified as atomic sulfur.

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Registry No. CdS, 1306-23-6; Nafion, 39464-59-0.

Search for Stationary Points on Surfaces

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Algorithms for finding local minima, maxima, and saddle points on surfaces, starting from an arbitrary point, are presented. These algorithms are based on making a local approximation to the surface in the form of a rational function constructed from the local first and second derivatives of the surface. All parameters of these algorithms required for stepping across the surface are determined in nonarbitrary ways. The convergence of these procedures to the desired stationary point is shown to be quadratic. Applications for stationary-point searches on two model surfaces are also given for illustrative purposes.

Introduction

Finding stationary points (minima, maxima, and saddle points) on energy surfaces is important in chemical physics because they correspond to equilibrium geometries and transition states and because the classical equations of motion connecting such points can be used to describe the reaction dynamics. For a surface $E(x_1, \dots, x_n)$ depending on independent variables $\{x_i\}$, a stationary point is characterized by $\partial E/\partial x_i = 0$, that is, by vanishing slopes for all variables. In addition, a minimum corresponds to a point having positive curvatures $\partial^2 E/\partial x_i^2 > 0$, for all variables and a maximum has $\partial^2 E/\partial x_i^2 < 0$. For a saddle point of order μ , there exist μ variables relative to which the curvature is negative; it is positive relative to the remaining $(n - \mu)$ variables. In molecular quantum chemistry the ab initio determination of first and second derivatives of the energy with respect to geometric variables, though laborious, is within reach.¹ An algorithm that systematically and efficiently locates stationary points starting from an arbitrary point and using local first- and second-derivative information is given in this paper.

There exists extensive literature in numerical analysis regarding the search for extrema on multidimensional surfaces. References 2-6 describe techniques for minima and saddle point searches.

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The highlights of the algorithm presented here are that all optimization parameters are calculated in an ab initio manner and the procedure is quadratically convergent with the stability characteristics of a saddle-point search being the same as those of a local-minimum search.

General Discussion

For a surface of n independent variables, the Taylor expansion allows one to explore the neighborhood of a point x_0

$$E(\mathbf{x}) = E_0 + \mathbf{g}^T \mathbf{x} + \frac{1}{2} \mathbf{x}^T \mathbf{H} \mathbf{x} + \dots \quad (1)$$

Here the step vector $\mathbf{x} = (x_1, \dots, x_n)$ gives the displacement away from x_0 , the gradient vector \mathbf{g} and hessian matrix \mathbf{H} contain elements of first and second derivatives of E with respect to the (x_i) calculated at x_0 . The Newton-Raphson (NR) procedure allows one to step toward a stationary point of E , near x_0 by approximating the expansion of eq 1 in the neighborhood of x_0 quadratically

$$\epsilon = E(\mathbf{x}) - E_0 = \mathbf{g}^T \mathbf{x} + \frac{1}{2} \mathbf{x}^T \mathbf{H} \mathbf{x} \quad (2)$$

and imposing the stationary requirement $\partial \epsilon / \partial x_i = 0$, giving

$$\mathbf{H} \mathbf{x} + \mathbf{g} = 0 \quad (3)$$

To facilitate the analysis of the NR algorithm and those developed in this paper, without any loss of generality, it is useful to transform to new displacement variables in which the Hessian matrix is

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