

Surface Spectroscopy of Platinum-Cadmium Sulfide-Perfluorosulfonate Polymer Systems

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Films on Pt/CdS/Nafion have been constructed for use in investigations of photoassisted H_2 production from H_2O . These films were characterized using scanning electron microscopy, x-ray photoelectron spectroscopy and x-ray diffraction. Induction periods, observed in the photoassisted H_2 production, correlate with the extent of reduction of partially oxidized Pt to Pt^0 as measured by the Pt(4f) binding energy changes. Two crystal forms of CdS (cubic and hexagonal) were detected by x-ray diffraction. The scanning electron micrographs show that samples dominated by the cubic form have a very rough surface compared to the hexagonal form. The S(2p) binding energies indicate that the surface of the hexagonal form is rich in sulfate ion, whereas the surface of the cubic form is dominated by sulfide ion.

Over the past several years, interest in photoassisted reactions involving semiconductors has expanded (1). Among the interesting relatively small bandgap materials is CdS (bandgap=2.4 eV). In operating systems, CdS has been stabilized with respect to photodecomposition by the addition of sacrificial reagents (2). Recently, the cleavage of water in a colloidal CdS/Pt/RuO₂ system has been reported (3) and has led to increased interest in this system (4).

While these colloidal systems are very interesting, another approach with considerable promise involves localizing the photoactive species and other catalytic components in a polymer membrane. This has recently been accomplished for CdS in polyurethane (5) and Nafion (6). This kind of system lends itself to characterization using surface analytical techniques while at the same time preserving many of the small particle features of colloids. In this paper we examine how the CdS crystal structure and the state of the Pt in a CdS/Pt/Nafion system influences the rate of hydrogen generation in a system containing a sacrificial electron donor, S^{2-} . A detailed account of the photoassisted H_2 production rates is given elsewhere (6b).

NOTE: Nafion is Du Pont's brand name for perfluorosulfonate polymers.

Experimental

Platinum was added to Nafion before incorporating CdS in order to avoid the reduction of CdS during the platinization process. Nafion (DuPont 117, 0.018 cm thick) films were soaked in $\text{Pt}(\text{NH}_3)_2\text{I}_2$ (0.1 mM) solution for 4 hr. The amount of the Pt complex incorporated was determined by measuring the optical absorption change in the liquid phase. The films were subsequently reduced with NaBH_4 (0.1 M) solution for one day to produce Pt metal dispersed throughout the polymer film. The amount of Pt was found to be about 0.02 mg cm^{-2} .

CdS was incorporated into these platinized films using two methods. In the first, the film was soaked in a $\text{Cd}(\text{NO}_3)_2$ (0.5 M) solution for 1 hr, washed with water, soaked in boiling HNO_3 (0.03 M, pH=2.1) solution, treated with bubbling H_2S for 10 min and finally washed with boiling water. The resulting films were bright orange.

In the second method, the preparation differed only in the H_2S treatment which was carried out at room temperature in distilled water. In both cases the amount of CdS incorporated was determined by polarographic reduction of Cd^{2+} to be 1.3 mg cm^{-2} .

The photodriven production of hydrogen was carried out using 1 cm x 1 cm films in a 10 ml Pyrex test tube containing 3 ml of 0.1 M Na_2S solution (pH=13). Prior to irradiation, these solutions were degassed by bubbling N_2 through them. Irradiation was done with a 1 kW Xenon lamp. The light was filtered through water to remove most of the IR radiation. The amount of hydrogen formed was measured with a gas chromatograph.

The films were characterized using x-ray powder diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The photoelectron spectroscopy utilized a Vacuum Generators ESCA Lab II system with $\text{Mg}(\text{K}\alpha)$ radiation. Binding energies (BE) were measured with respect to the surface C(1s) peak (284.5 eV) which was always present in these films. Scanning electron microscopy was done with a JEOL JSM-35C system.

Results and Discussion

Pt/CdS/Nafion. Figure 1 shows the time dependence of the evolution of hydrogen for the irradiated films. The first preparation method gives the hexagonal form (7). In both cases x-ray linewidth analysis indicates particle sizes of 20 nm. The H_2 generation rate is at least three times faster for the cubic form than for the hexagonal form. Generally speaking, the XRD and SEM analysis indicates small particles of CdS and Pt in intimate contact.

Figure 1 also shows an induction period during which the rate of H_2 production accelerates. Although this effect is more pronounced for the hexagonal CdS sample, it is present in both. Further results, summarized in Fig. 2, emphasize this induction period. The curves labelled (1) and (2) involved repeated use of the same film. Between runs (1) and (2) the film was washed in boiling water. Clearly the rate of H_2 evolution was significantly faster in the second run. Repeated experiments gave data superimposable on curve (2).

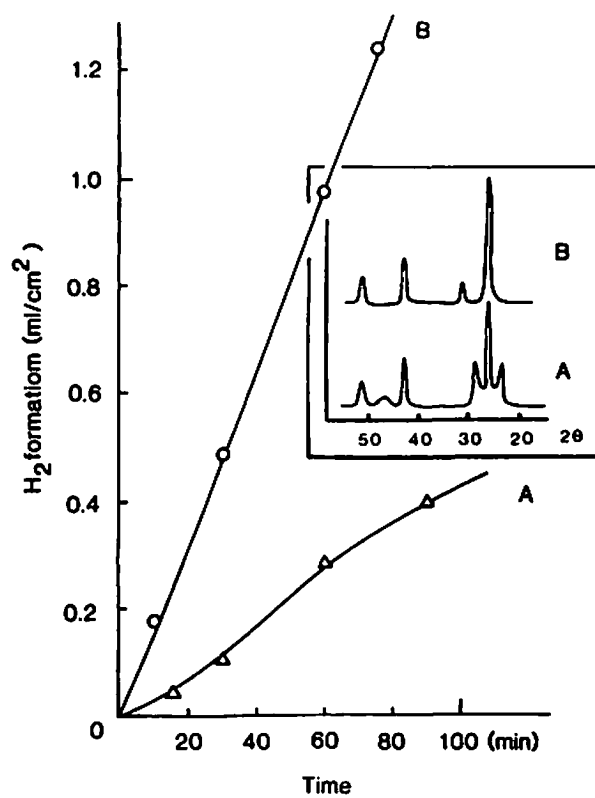


Figure 1. Comparison of H₂ generation from platynized hexagonal CdS (curve A) and cubic CdS (curve B) in Nafion 117. The insert shows x-ray powder diffraction spectra of CdS in these films.

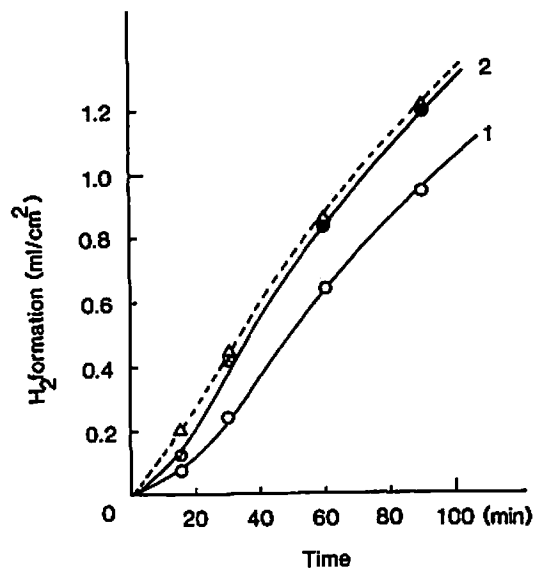


Figure 2. Time dependence of hydrogen production in a 1 cm² Nafion film containing CdS (1.3 mg cm⁻²) and Pt (0.02 mg cm⁻²). Curves (1) and (2) are repeated runs with the same film. The dashed curve is for a different film pretreatment. See text for details.

In another experiment, a new film was pretreated by bubbling H_2 at 1 atm and 300 K through the solution for 0.5 hr prior to the N_2 treatment described above. The activity of this film is shown in Fig. 2, dashed curve. It is closer to (2) than (1), and the induction time is relatively short. This indicates that, during the initial stages of irradiation with a fresh film, the activity is enhanced by some process involving hydrogen.

Similar results have recently been reported by Aspnes and Heller (8). They proposed an autocatalytic model for photoactive systems involving metal/compound semiconductor interfaces. To explain induction times in CdS systems (9), they suggest that hydrogen incorporated in the solid lowers the barrier to charge transfer across the interface and thereby accelerates H_2 production rates.

While our results follow the same trend and may involve similar effects, surface analysis using XPS indicates that the oxidation state of Pt is also significant. The Pt(4f) binding energy was 72.1 eV on fresh films. After irradiation in the manner described above, the BE dropped to 71.3 eV. For a Pt foil, the measured BE was 71.2 eV. We conclude that whole Pt was partially oxidized in the fresh films and that during the early stages of hydrogen production, it was reduced to Pt^0 . This change in oxidation state is, we believe, related to the change in H_2 production activity.

To investigate this further, we probed the state of Pt before CdS incorporation into the film. After Pt incorporation and reduction with $NaBH_4$, the Pt(4f) BE was 71.1 eV, indicating that Pt^{2+} complexes were completely reduced to Pt^0 . Pt in films without CdS can be oxidized by boiling in nitric acid as indicated by the films becoming clear. Thus, the oxidized Pt species present in fresh CdS/Pt/Nafion films is formed at some point during the CdS incorporation process. Thus, while not excluding the process proposed by Aspnes and Heller (8), we consider the reduction of partially oxidized Pt as responsible, in part, for the observed induction period (10).

CdS/Nafion. Scanning electron microscopy (SEM) of the CdS films prepared by both methods revealed a striking difference in the surface roughness of cubic and hexagonal CdS in Nafion (Fig. 3). Examination of a cross-sectioned film by SEM did not show any morphological differences in the two crystal forms in the interior of the Nafion. X-ray fluorescence demonstrated that Cd was distributed throughout the Nafion, with a slightly higher concentration near the outer surface (Fig. 3).

The XPS of the Cd(3d) region shows (Fig. 4) that the cubic CdS film has a Cd(3d_{5/2}) BE of 405.6 eV, while the hexagonal CdS film has a peak at 406.4 eV. After Ar^+ bombardment for a short time of the hexagonal CdS film, the peak position does not shift but the integrated intensity increases.

Figure 5 shows XPS for the S(2p) region. The cubic CdS film has peaks at 161.7 and 168.9 eV. Hexagonal CdS has only one peak at 169.6 eV which after Ar^+ bombardment decreases in intensity and broadens. Based on a systematic comparison with binding energies reported on a variety of cadmium and sulfur compounds (11), we assign the Cd(3d_{5/2}) 405.6 eV peak to Cd^{2+} ion of CdS and the S(2p) 161.7 eV peak to S^{2-} ion of CdS.

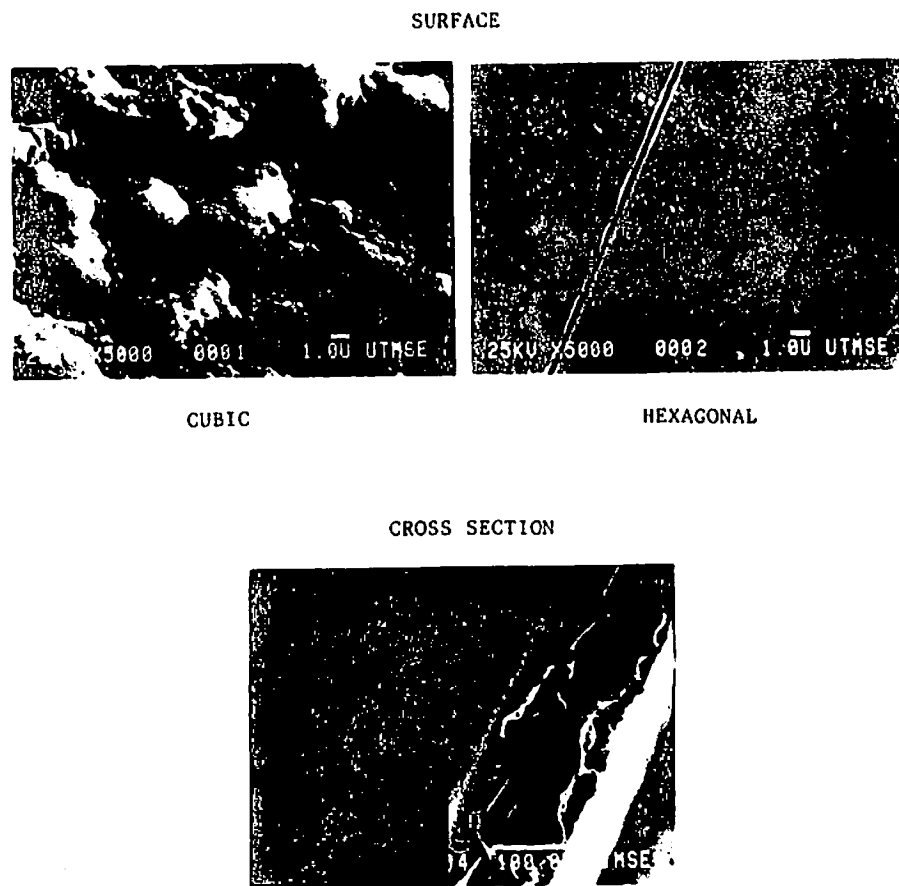


Figure 3. SEM photographs of hexagonal CdS/Nafion and cubic CdS/Nafion.

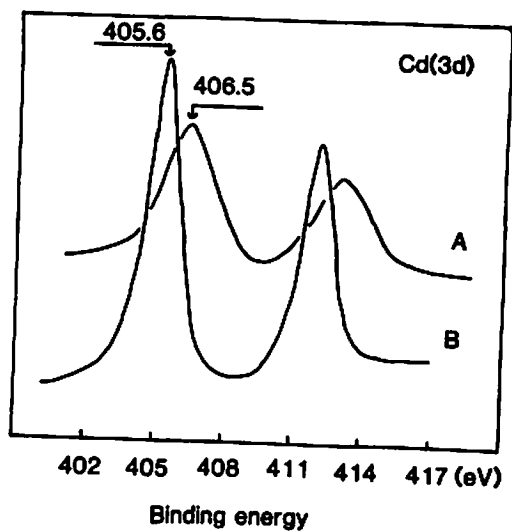


Figure 4. Cd(3d) XPS spectra of hexagonal CdS/Nafion (A) and cubic CdS/Nafion (B) films.

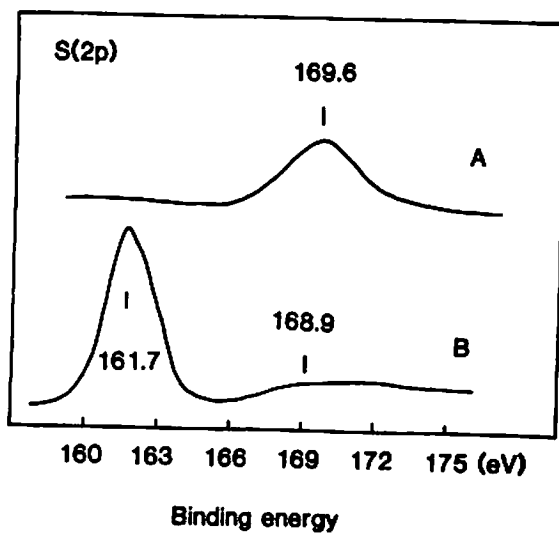


Figure 5. S(2p) XPS spectra of hexagonal CdS/Nafion (A) and cubic CdS/Nafion (B) films.

To elucidate the higher BE peaks [S(2p) 168.9, 169.6 eV], we examined the Nafion film itself because it has $-\text{SO}_3^-$ cation exchange sites. Only C(1s) and F(1s) peaks were observed. No S(2p) peak was observed even after Ar^+ bombardment. This result suggests that the surface concentration of cation exchange sites involving $-\text{SO}_3^-$ is low. Sulfur located well below the surface would, of course, not be detected by XPS. We assign the higher BE S(2p) peak to a surface sulfate species (11).

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 CdS than the hexagonal film. In both, the C(1s)/F(1s) ratio is similar to Nafion itself.

The higher BE for the Cd(3d) peak for the film containing hexagonal CdS can be understood in terms of surface charging of the sample under x-ray irradiation. Since the surface of the hexagonal sample is not as rich in CdS as the cubic sample, we expect the Nafion to play a greater role in the former, and this would lead to a great surface charge. Shifts to higher BE and extensive broadening would then be expected, as observed. This conclusion based on XPS is consistent with the SEM data. We conclude that the surface density of CdS is higher for the cubic CdS and that the hexagonal CdS film surface contains a large amount of sulfate ion. One can speculate that the presence of sulfate may contribute to the lower activity of the hexagonal form for the photoassisted production of hydrogen.

Table I. XPS Peak Ratios

(a)	α -CdS	β -CdS
Cd(3d _{5/2})/F(1s)	0.04	8.4
S(2p)/F(1s)	0.02 ^(b)	1.6
C(1s)/F(1s)	0.1	0.1

(a) Nafion F(1s) peak was used as standard.

(b) This peak was assigned to SO_4^{2-} species.

Acknowledgments

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