Photocatalytic Hydrogen Evolution with Platinum Loaded Cadmium-Iron-Sulfide Mixed Crystal Powders in Aqueous Media

Chullae Cho, Sejin Park, and Hasuck Kim*

Division of Chemistry and Molecular Engineering, Seoul National University, Seoul 151-742, Korea
Received July 4, 2000

Mixed crystal powders based on Cd, Fe, and S have been synthesized by varying the ratio of CdS and FeS_2 in order to find a suitable material useful for the effective conversion of solar energy. Hydrogen gas was evolved only with CdS/Pt by photocatalytic reaction under white light in an aqueous 1 M sodium sulfite solution. From electrochemical studies of semiconductor electrodes, it was shown that the onset potential shifted to the positive direction and that the bandgap energy also decreased as the molar ratio of Fe increased. A hydrogen evolution mechanism in terms of the conduction band potential and hydrogen evolution potential is proposed.

Introduction

The photoelectrochemistry of semiconductors, which is associated with solar energy application and photochemical energy conversion has been one of the most extensively studied fields.[1] Moreover, most studies were on hydrogen evolution because of its potential value as a clean fuel in the next century.[2] Recently, environmental concerns and replacing fossil fuel are introducing a renewed interest in hydrogen evolution from photoelectrolysis of water.

When a semiconductor electrode absorbs photons with an energy greater than its bandgap, electrons can be excited to the conduction band, thus creating electron-hole pairs.[3] In the case of an n-type semiconductor, the electric field drives photogenerated holes toward the interfacial region and electrons toward the interior of the electrode. Such photogenerated holes and electrons can participate in a redox reaction with various chemical species. Hydrogen evolution results from the reduction of water by electrons. It is well known that the reducing ability of electrons in a highly doped semiconductor depends mainly on the energy level of the conduction band.[4]

At the moment, semiconductor materials are not satisfactory in photocatalytic reactions because of their lack of stability and low efficiency for solar energy conversion. CdS has been used most often for hydrogen evolution from water, but the bandgap (2.4 eV) is too large to utilize the spectrum of sunlight effectively.[5,6] On the other hand, even though FeS$_2$ has several advantages such as suitable energy gap (0.95 eV), high absorption coefficient (6×10^5 cm^{-1} for $h\nu \geq$ 1.3 eV), large natural abundance and low cost.[7] it turned out that it is not an effective catalyst for hydrogen evolution. Physical and chemical properties of FeS$_2$ were rather similar to those of CdS.

For efficient solar energy conversion and hydrogen evolution, Tsubomura[8] and Tributsch *et al.*[9] have suggested cluster materials such as $CdS_{1-x}Se_x$. This prompted us to study the mixed crystals of the Cd-Fe-S system. In this paper, we report on the electrochemical characterization and hydrogen evolution of mixed crystals loaded with Pt to form micro-photocells.

Experimental Section

CdS (98%) and FeS$_2$ (99.9%, -100 mesh) were purchased from Aldrich Chemical Co. and used without further purification. The crystal structure of CdS was amorphous and the particle size was about 0.05 μm. The crystal structure of FeS$_2$ was cubic. Other chemicals were all reagent grade. Solutions were prepared with triply distilled water (Nanopure II, Barnstead, Boston, MA). The pH of the solution was adjusted to 8.0 by adding boric acid, because the mixed crystal powders were soluble in both strong acid and base solutions.

Cd-Fe-S powders were prepared by grinding CdS and FeS$_2$ in an agate mortar and heating at 700 °C for 48 h under nitrogen condition in an electric furnace. The molar ratio of each element was controlled by varying the molar ratio of CdS and FeS$_2$. The molar ratio of the mixed crystal powder was obtained by analyzing the dissolved solution with an ICP spectrophotometer (Plasmascan 8410, Labtam Co. Australia). The Cd-Fe-S mixed crystal powders were loaded with Pt powder (3 wt%) by extensive shaking. Electrochemical measurement setup is shown in Figure 1. Also the semiconductor pellet electrode is shown in the Figure.

Photocatalytic hydrogen evolution was measured with a water jacketed 90-mL glass flask at 25$\pm$0.2 °C instead of the electrochemical measurement cell shown in Figure 1. The photocatalytic cell contains 20 mL of aqueous solution of 1 M sodium sulfite and 100 mg photocatalyst. This suspension solution was purged with N$_2$ for 30 min. The flask was gas-tight with a cap made of a silicone septum, and the photocat-
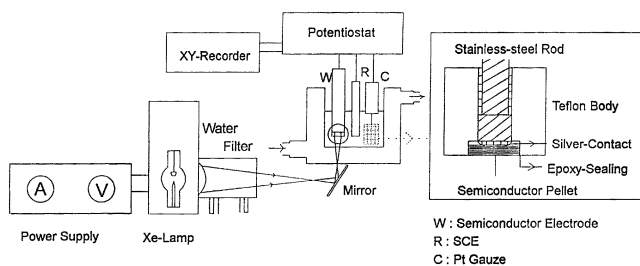

Figure 1. Schematic setups of photoelectrochemical experiment.

alytic reaction was studied under illumination with a 600 W xenon arc lamp (Oriel, Stratford, CT) of white light through water filter. The amount of hydrogen gas was measured with a gas chromatograph (Hewlett-Packard, HP5890A).

Pellets of CdS, FeS_2 and mixed crystal materials were made at a pressure of 150 Kg/cm^2 for 1 min. Pellets of mixed crystal materials were heated at 700 °C for 5 h under nitrogen condition. Thickness and diameter were about 1 mm and 13 mm, respectively. The electrochemical characterization of these pellets were made in a three-electrode cell with a platinum gauze counter electrode and a saturated calomel reference electrode. Potentiostatic analysis of the semiconductor working electrode was carried out with a PAR electrochemistry system consisted of models 173 and 175 (EG &G, Princeton Applied Research Corp., Princeton, N. J.).

X-ray diffraction patterns of the semiconductor powder were obtained with a Geigerflex diffractometer (Rigaku, Japan) using Cu-Kα radiation.

The bandgap of semiconductors was measured by plotting wavelength versus photocurrent obtained under the illumination with a Xe arc lamp (Farrand Optical Co. Inc., 150 W) and a Nernst glower with monochromator (Shimadzu Co. Japan).

Results and Discussion

In Figure 2, XRD patterns of pure CdS(a), pure FeS_2(e), and a mixture of CdS and FeS_2 powder(b) without heat treatment are shown, which denote the amorphous structure of CdS, the cubic structure of FeS_2, and the mixed structure of amorphous CdS and cubic FeS_2, respectively. Original peaks of the CdS phase of hexagonal crystal structure can be seen and additional peaks probably due to the presence of $Cd_{1-x}Fe_xS$ start to appear by heating at 700 °C for 2 h(c). Peaks due to FeS_2 are not observed in 2θ values between 20° and 70°. After heating at 700 °C for 48 h(d), only new peaks are clearly observed. Here, we are able to observe the CdS peaks changed to hexagonal lattice (marked as o) and some unexpected peaks (marked as x) due to FeS. To identify
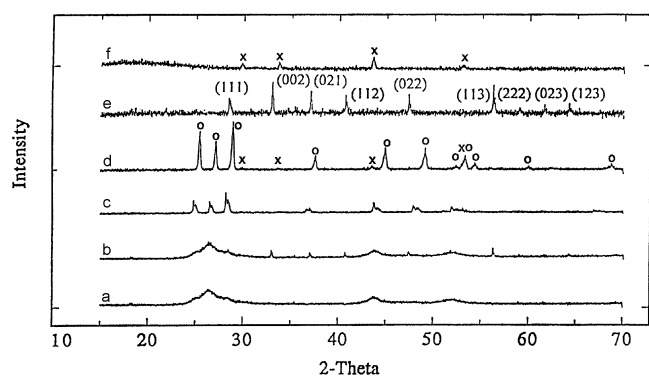
Figure 2. XRD patterns of $Cd_{0.41}Fe_{0.59}S$ semiconductor with various heat treatments: none(b), at 700 °C for 2 h(c), and at 700 °C for 48 h(d). Pure CdS without heat treatment(a). pure FeS_2 without heat treatment(e) and FeS_2 heated at 700 °C for 48 h (decomposed to FeS) (f).
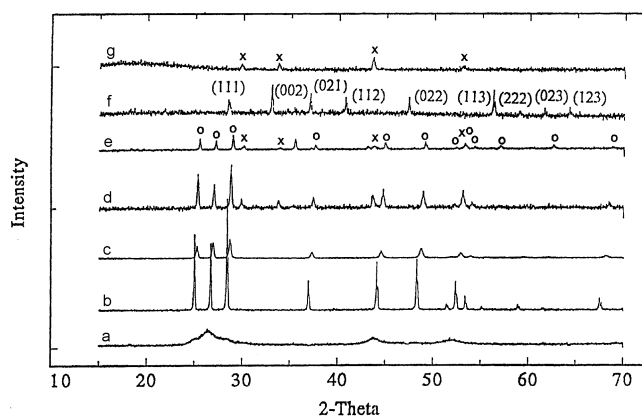
Figure 3. XRD patterns of $Cd_{0.72}Fe_{0.28}S$(b), $Cd_{0.53}Fe_{0.47}S$(c), $Cd_{0.17}Fe_{0.83}S$(d). and $Cd_{0.07}Fe_{0.93}S$ at 700 °C for 48 h(e). Pure CdS without heat treatment(a). pure FeS_2 without heat treatment(f), and FeS_2 heated at 700 °C for 48 h (decomposed to FeS) (g).

these peaks, FeS_2 powders of 0.1 g were heated under nitrogen condition at 700 °C for 48 h. Its XRD patterns(f) corresponded well to these peaks. Jovanovic[10] reported that the thermal decomposition of FeS_2 in a nitrogen atmosphere was proceeded as following:

$$2FeS_2 \rightarrow 2FeS + S_2$$
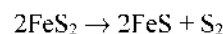
Heated FeS_2, therefore, must be FeS. Excess FeS_2 which is not participated to form a solid solution with CdS decomposes to FeS. The atomic composition of this crystal powder is determined as Cd : Fe : S = 0.41 : 0.59 : 1. However, the atomic composition is not critical due to the presence of FeS. Different 2θ values have been obtained as the molar ratio of Cd, Fe and S changes. (Figure 3) From XRD patterns, the critical point of solid solution is obtained when the x value in $Cd_{1-x}Fe_xS$ is about 0.5. The lattice parameters of the CdS plane decreased linearly as the x ($1 \geq x \geq 0$) increased. These results indicate that solid solutions seem to form by heat treatment at 700 °C for 48 h.

The bandgap energy is determined by varying the longest wavelength which produces an anodic photocurrent at the electrode held at a saturation potential. Figure 4 shows that the onset potential of anodic photocurrent shifts to the longer wavelength as the molar ratio of Fe in the mixed crystal powder increases. The bandgap energy of a series of mixed crystal with different Fe content from zero (pure CdS) to unity (pure FeS_2) decreases from 2.36 eV to 0.95 eV.

The amount of hydrogen gas evolved by the photocatalytic reaction of CdS/Pt with white light illumination for 10 h is determined as 50 μmol. With Cd-Fe-S mixed crystal powders, no hydrogen gas is detected.

In order to explain these results, photoelectrochemical measurement was carried out to find the relationship between the flatband potential of semiconductor material and hydrogen evolution potential.

Figure 5 shows the i-v curves of semiconductor electrodes used in this study. As the molar ratio of Fe in the mixed crystal powder increases, the onset potential shifts to the positive direction. The onset potential of CdS is -1.09 V. In the
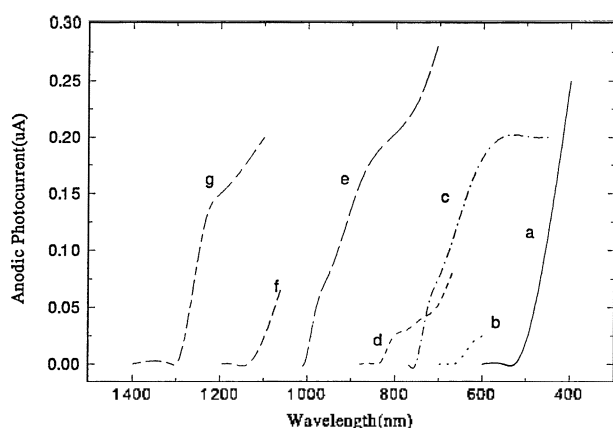
Figure 4. Effect of wavelength on photocurrent. CdS(a). Cd$_{0.72}$Fe$_{0.28}$S(b). Cd$_{0.53}$Fe$_{0.47}$S(c). Cd$_{0.41}$Fe$_{0.59}$S(d). Cd$_{0.17}$Fe$_{0.83}$S(e). Cd$_{0.07}$Fe$_{0.93}$S(f). and FeS$_2$(g). Solution: aqueous 1 M sodium sulfite (pH 8.1).

Figure 6. Potential of the conduction band edge of Cd-Fe-S depending on the molar ratio of Fe. Hydrogen evolution potential is also shown for comparison. Solution: aqueous 1 M sodium sulfite solution (pH 8.1).
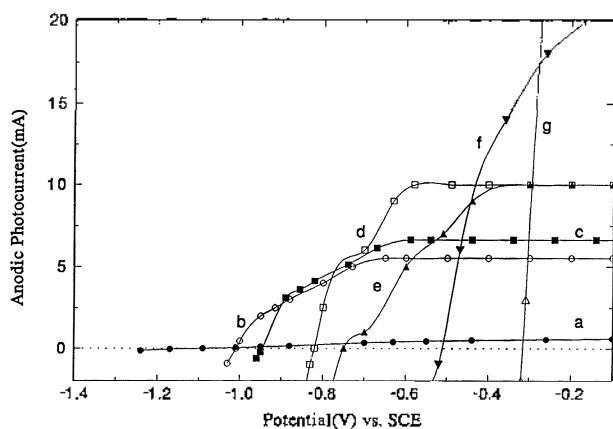

Figure 5. Anodic photocurrent vs. potential for Cd-Fe-S mixed crystal powders. CdS(a). Cd$_{0.72}$Fe$_{0.28}$S (b). Cd$_{0.53}$Fe$_{0.47}$S (c). Cd$_{0.41}$-Fe$_{0.59}$S (d). Cd$_{0.17}$Fe$_{0.83}$S(e). Cd$_{0.07}$Fe$_{0.93}$S(f). and FeS$_2$(g). Solution: aqueous 1 M sodium sulfite (pH 8.1). Electrode area: about 20.4 mm^2.

$$V_{c.s} - V_{fl} - (E_c - E_f)/q$$

where $V_{c.s}$, V_{fl}, E_c, E_f and q is the conduction band edge, flatband potential, conduction band level, Fermi level and electron charge, respectively. If a semiconductor is rather highly doped, the difference between the Fermi level and the bottom of the conduction band is negligibly small.[12] Therefore, the conduction band edge and flatband potential are almost equal. The doping level of mixed crystal semiconductors used in this study is very high, so these levels are probably equal. Therefore, the flatband potential can be obtained from the Butler equation.[13] Both CdS and FeS$_2$ are proved as n-type semiconductors from respective i-v curves.

Hydrogen gas is not evolved by the photocatalytic reaction except in the case of CdS. This can be explained by taking into account the fact that the conduction band of mixed crystal powder and that of FeS$_2$ are very close and lie under the hydrogen evolution potential. Tsubomura *et al.*[8] have explained the reason why CdSe(an inactivite catalyst for hydrogen evolution, $E_g = 1.7$ eV) electrode of CdS$_{1-x}$Se$_x$ does not evolve hydrogen, as the conduction band of CdSe situates closely to the hydrogen evolution potential. This is in accordance with the results of our experiment. They also have prepared CdSe-ZnSe mixed powder[8] by incorporating ZnSe ($E_g = 2.7$ eV) which has negative conduction band potential compared with CdSe, expecting that ZnSe would change the conduction band potential of CdSe. The conduction band potential of the mixture, however, is not more negative than that of CdSe.

The photocatalytic reaction with mixed crystals is carried out in H$_2$O : EtOH (vol. 1 : 1) solution, but hydrogen gas is not evolved. Ethanol is not decomposed by this photocatalytic reaction. Therefore, cadmium-iron-sulfide compounds are catalytically inactive for hydrogen evolution. It is unlikely that the electrons on Pt surface are used by reactions other than the reduction of water, which is under investigation.

Acknowledgment. This work was financially supported by the KOSEF through the Center for Molecular Catalysis, Seoul National University.

case of CdS, the increase in pH shifts the onset potential to the negative direction. This is the same trend as the hydrogen evolution that potential shifts to the negative direction by increasing the pH. The mixed crystal powder with a higher Fe content produces a larger saturation photocurrent in the positive scan. This is directly related to the bandgap of the electrode. Because the absorption wavelength of a semiconductor with a narrow bandgap is broad, such a semiconductor absorbs a large number of photons and there are many photogenerated electrons in the conduction band. In Figure 5, an enormously large photocurrent from FeS$_2$ is observed in the positive potential scan compared to the CdS semiconductor. Energy conversion efficiency of FeS$_2$ and mixed crystal semiconductors have significantly increased, although no hydrogen gas is evolved by cathodic photocatalytic reaction. This indicates that the mixed crystals are n-type seminconductors.

Figure 6 shows the variation of flatband potential by molar fraction of Fe. The conduction band edge can be expressed as the following equation[11]
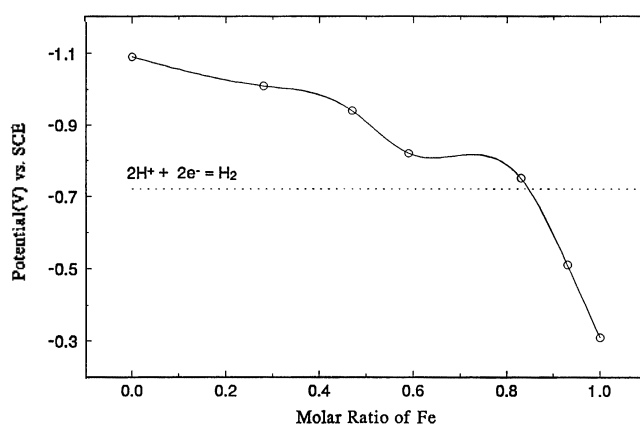
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