Bipolar cadmium selenide/cobalt(II) sulfide semiconductor photoelectrode arrays for unassisted photolytic water splitting

E. S. Smotkin, S. Cervera-March, A. J. Bard, A. Campion, M. A. Fox, T. Mallouk, S. E. Webber, and J. M. White

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explain why HSO_3^- ions are formed on Na–Y zeolite only at higher degrees of hydration.

Our UV/visible spectroscopic studies indicated that HSO_3^- ions, formed on the surface of Na–X (or Na–Y) zeolite, are highly reactive toward hydrogen sulfide. After adsorption of SO_2, followed by desorption of all SO_2 species more weakly held than

HSO_3^-, and interaction with H_2S, we observed UV/visible bands typical of Claus reaction products. This again confirmed that HSO_3^- anions, formed via chemisorption of SO_2 in the presence of traces of water, were active intermediates in the Claus reaction.

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Bipolar CdSe/CoS Semiconductor Photoelectrode Arrays for Unassisted Photolytic Water Splitting

E. S. Smotkin, S. Cervera-March, A. J. Bard,* A. Campion, M. A. Fox, T. Mallouk, S. E. Webber, and J. M. White

Department of Chemistry, The University of Texas, Austin, Texas 78712 (Received: July 23, 1986)

Bipolar CdSe/CoS semiconductor photoelectrode panels, capable of vectorial electron transfer, have been used in series arrays to photodecompose water to yield hydrogen and oxygen in stoichiometric ratio with a maximum equivalent solar efficiency of about 1%. The use of bipolar photoelectrode arrays obviates the problems of the location of the semiconductor band edges relative to the water decomposition potentials and the requirement of semiconductor stability during photohole generation and oxygen production in aqueous solutions.

Introduction

We demonstrate here the use of a small bandgap semiconductor, CdSe, for the unassisted photodecomposition of water to yield the separated products hydrogen and oxygen in the stoichiometric ratio of 2:1, with a novel arrangement of bipolar semiconductor photoelectrodes. Direct water splitting in an n-type semiconductor photoelectrochemical (PEC) cell is usually thought to require a semiconductor that is stable under irradiation in aqueous solution and whose valence band is located at sufficiently low energies (positive potentials) that oxidation of water is thermodynamically and kinetically possible. Thus, n-TiO_2 and n-$SrTiO_3$ have been used. Fujishima and Honda[1] chose TiO_2, although the large bandgaps (≥ 3 eV) greatly limit the solar efficiency of such PEC cells. Smaller bandgap semiconductors, such as metal chalcogenides, often undergo deleterious photoanodic decomposition when illuminated in solutions where direct oxidation of water is possible. For example, CdSe undergoes photodecomposition according to

$$CdSe + 2h^+ \rightarrow Cd^{2+} + Se \qquad (1)$$
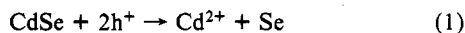
and the photocurrent decays as an insulating layer of elemental selenium forms on the semiconductor surface. Metal chalcogenides, such as CdS and CdSe, can be stabilized by the use of a polysulfide electrolyte.[2] In such systems, oxidation of sulfide ion prevents lattice oxidation. Thus, while a photovoltaic cell that employs a n-CdSe photoanode and suitable electrocatalytic cathode for polysulfide reduction (e.g., CoS, PbS, sulfurized brass) is capable of sustained electrical current generation, it cannot split water into hydrogen and oxygen in the presence of polysulfide.

We have recently described the use of a series array of bipolar TiO_2/Pt photoelectrodes capable of vectorial electron transfer.[3] These arrays permit unassisted photolytic water splitting with oxygen evolved at the semiconductor surface and hydrogen evolved on a platinum surface. As only UV light is absorbed by TiO_2,

the system is of limited efficiency with normal solar flux. However, it is also possible to use an array of bipolar electrodes with smaller bandgap semiconductors, e.g., CdSe/CoS, with stable end electrodes (e.g., Pt) for production of H_2 and O_2. A schematic diagram of this system is shown in Figure 1. The energetics of vectorial electron transfer at one bipolar photoelectrode are illustrated in the expanded view of the terminal photoelectrode, I/J, depicted in Figure 1. The basic principles of PEC devices have been discussed in detail.[4–6] The chemical reactions pertaining to each interface are given in Chart I.

CdSe thin films for PECs have been prepared by spray pyrolysis,[7] vacuum evaporation,[8] electrodeposition,[9] chemical bath deposition,[10] and slurry painting.[11] The bipolar electrodes used here were fabricated by the method of Hodes et al.,[11] by painting a slurry of CdSe on a titanium foil (0.025 mm thick) annealing in air at 500 °C followed by photoannealing in 0.1 M H_2SO_4. Annealing in the absence of oxygen resulted in panels with very poor open circuit voltages and short circuit currents. The beneficial effect of air annealing has been reported by others.[10,12] CoS was then electroplated on the back side of the titanium foil. The electrode (A,B) was made by sputter-depositing platinum on one side of titanium foil and electroplating CoS on the opposite side. The terminal photoelectrode (I,J) was made by painting and annealing a slurry of CdSe on titanium foil which had been previously sputter-deposited with Pt on the opposite side.

All CdSe semiconductors in the array were in contact with a stabilizing polysulfide solution and only the two terminal Pt electrodes contacted 2 M KOH and were connected to each other by a KOH salt bridge. Oxygen was evolved at the Pt face of the

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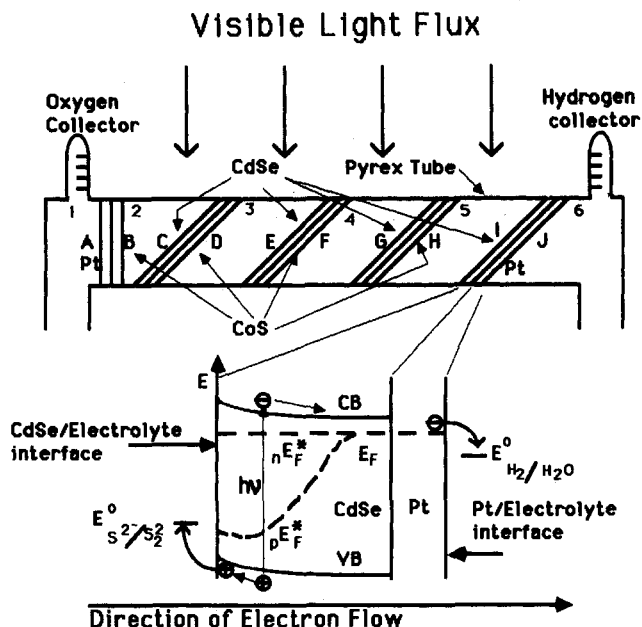(11) Hodes, G.; Cahen, D.; Manassen, J.; David, M. *J. Electrochem. Soc.* **1980,** *127,* 2252.
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Visible Light Flux

Figure 1. Schematic of water photoelectrolysis cell. Expansion shows energetics of bipolar panel. A,J: Pt; B,D,F,H: CoS; C,E,G,I: CdSe. Solutions: 1, 6: KOH (1 M); 2–5: Na_2S (1 M), S (1 M), KOH (1 M). For H_2 and O_2 generation solutions 1 and 6 are connected with KOH bridge.

Pt/CoS electrode while hydrogen was evolved at the Pt face of the CdSe/Pt electrode. The relevant current–potential (i–V) data for a CdSe/CoS panel are shown in Figure 2. Curve A is the i–V characteristic for the dark reduction of polysulfide on the CoS electrodes. The photooxidation of sulfide on the semiconductor surface is shown on curve B. The irradiation source was a Xe lamp with an 8-in. water filter. The equivalent solar power was determined by calculating the total solar flux required to obtain the bandgap light provided by the xenon lamp. The open circuit voltage, V_{oc}, is 0.5 V with a short circuit current, i_{sc}, indicated by the dotted line placed so that the magnitude of the anodic current (curve B) is equal in magnitude to the cathodic current (curve A) of 12 mA/cm^2.

The power characteristics of a six photoelectrode PEC array were evaluated by employing a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat with a PAR Model 175 universal programmer as a variable load.[3] The potential of a CdSe surface under illumination with a xenon lamp was adjusted from 0 V relative to a CoS electrode (to yield i_{SC}) to negative potentials until the current ceased (to yield the V_{oc}). The results are shown in the inset of Figure 2. As with the TiO_2 system, the open circuit photovoltages are additive, the sum of the series being in excess of 2.5 V. At higher light fluxes the open circuit voltage of a single panel was in excess of 0.6 V.

The fill factor, ff, for the series array was 0.57. The efficiency for electrical power generation measured for six photoelectrode panels was 1.9% as calculated by

$$\eta e = (V_{oc}i_{sc}(\text{ff}))/(W_L NA) \tag{2}$$

where W_L is the equivalent solar light flux incident on the cell, N is the number of photopanels (6), and A is the projected area of a panel (the light flux is directed 45° off the normal of the panels). If a correction is made for the absorption of light by the polysulfide solution, the efficiency is 5.3%. Hence, with the given quality of the panels used here, improvements can be made in the system efficiency up to 5.3%.

When the Pt faces were contacted by KOH and connected by a KOH bridge, as shown in Figure 1, hydrogen and oxygen ev-
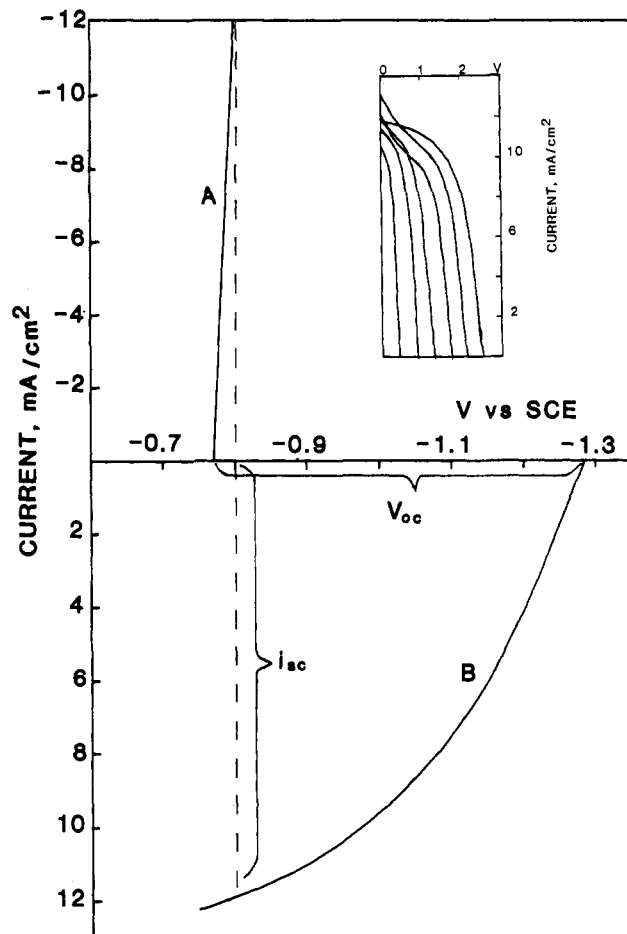
Figure 2. Current–potential characteristics of a CdSe//CoS panel in 1:1:1 M KOH:S:Na$_2$S solution. Curve A: polysulfide reduction on dark CoS surface. Curve B: oxidation of polysulfide on illuminated CdSe surface. Effective solar flux: 67.0 mW/cm^2. Inset: power curves for water photoelectrolysis device used in water photolysis experiment with six photopanels and one dark CoS panel. Effective solar flux: 52.0 mW/cm^2. Projected area of each panel: 1.04 cm^2. V_{oc}'s are in order from left to right of panels 1 through 6 in series.

olution occurred. The photovoltage of the illuminated CdSe photoelectrode array induces bipolarity in the dark electrode A/B. Water photolysis experiments were carried out for 1-h periods without stirring. Upon illumination, bubbles immediately began streaming from the Pt surfaces. The identity of the gases evolved at the Pt cathode and anode, hydrogen and oxygen, respectively, was verified by gas chromatography. After 1 h, the rate of bubble formation on the terminal Pt surfaces decreased. This may be caused by pH gradients developing at the Pt/KOH interfaces. That degradation was not due to effects at the CdSe or CoS interfaces was verified by removing the KOH bridge and obtaining power curves for electrical generation. No decay was observed in the power curves, hence decreased gas evolution is attributed to phenomena in the terminal cells. The stability of the internal array was further verified by measuring the photocurrent (xenon light, 266 mW/cm^2) of a three-electrode array across a 1-ohm resistor continuously for 100 h. The current decay was less than 4%. Replacement of the solution bridge restored hydrogen evolution to the initial rate (>1 cm^3/h), supporting the above conclusion. The hydrogen to oxygen volume ratio obtained in this study was 2.1 ± 0.3. The efficiency (calculated for light incident on the cell) for water photolysis was 0.32% calculated by

$$\eta_H = (R(\Delta G^\circ))/(W_L NA) \tag{3}$$

CHART I

A	Pt/KOH (2 M)
B, D, F, H	CoS/KOH (1 M), S (1 M) Na$_2$S (1 M)
C, E, G, I	CdSe/KOH (1 M), S (1 M) Na$_2$S (1 M)
J	Pt/KOH (2 M)

$$OH^- \rightarrow {}^1/_4O_2 + {}^1/_2H_2O + e^-$$
$${}^1/_2S_2{}^{2-} + e^- \rightarrow S^{2-} \text{ (dark)}$$
$$S^{2-} + h^+ \rightarrow {}^1/_2S_2{}^{2-} \text{ (light)}$$
$$H_2O + e^- \rightarrow {}^1/_2H_2 + OH^-$$

where R is the rate of hydrogen evolution (mol/s), and ΔG is the standard free energy change for the decomposition of water to hydrogen and oxygen (J/mol). If a correction is made for the light absorbed by the polysulfide solution, the efficiency was 0.91%. Further improvements can be made by using a better electrode with a lower overpotential for O_2 evolution than Pt (e.g., a nickel-based electrode[13]) and by using smaller bandgap material

either directly or as underlayers for larger bandgap materials in biphotonic tandem panels.[14] Such improvements, guided by computer modeling for maximizing efficiency, are currently under investigation in these laboratories.

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Calorimetric Study on the State of Aromatic Molecules Sorbed on Silicalite

H. Thamm

Academy of Sciences of the GDR, Central Institute of Physical Chemistry, GDR-1199 Berlin, Rudower Chaussee 5, GDR (Received: July 26, 1986; In Final Form: October 28, 1986)

Differential heats of sorption have been determined calorimetrically for benzene, toluene, ethylbenzene, and *p*-xylene on silicate as a function of pore filling. In all cases abrupt changes in the state of the sorbed molecules are observed when the amount sorbed exceeds 1 molecule per $^1/_4$ unit cell. While in the case of benzene, toluene, and ethylbenzene sorbate–sorbate interaction occurs only above 1 molecule per $^1/_4$ unit cell, the sorbed *p*-xylene molecules interact with each other below this loading.

Introduction

During the past few years several investigations on sorption equilibria of aromatic molecules on silicalite have been published. The experimental methods applied were gas chromatography,[1] measurements of sorption isotherms,[2–6] and measurements of sorption isochores (isosteres).[7] These investigations, however, were either restricted to relatively narrow ranges of pore filling and temperature or the experimental points were too widely spaced on the sorption or temperature scale, respectively, so as not to reveal possible changes of the derived thermodynamic functions of the sorbate within small intervals of loading and/or temperature.

This may explain that, contrary to ref 1–7, preliminary calorimetric results on the sorption of benzene and toluene on silicalite obtained in our laboratory[8,9] indicated considerably more complicated dependences of the differential heats of sorption on pore filling. Unfortunately, the silicalite sample used in these studies contained amorphous SiO_2 and did not allow for the deduction of exact quantitative relations between the heats of sorption and the sorbed amount. Moreover, the investigation of sorption equilibria on silicalite samples received from different laboratories led us to the conclusion that besides experimental care that has to be taken, as mentioned above, special attention must be paid to the chemical purity and the structural homogeneity of the

sample used. The presence even of minor quantities of framework Al, exchangeable cations, or structural OH groups has a significant influence on the sorption equilibria on silicalite or the isostructural ZSM-5 molecular sieves, respectively.[10]

Therefore it is important to note that the following results refer to a 100% crystalline silicalite sample of high chemical purity that corresponds to the end member of the ZSM-5 series with Si/Al approaching infinity.

To study systematically the energies of interaction of aromatic molecules on silicalite we investigated the sorption of benzene, toluene, ethylbenzene, and *p*-xylene. For comparison we also measured the differential heats of sorption of *n*-hexane on the same silicalite sample.

Experimental Section

The differential heats of sorption were measured by a Calvet-type microcalorimeter (Setaram) at 301 K. Both the thermokinetic curve of the calorimeter and the pressure in the gas phase were continuously recorded to ensure the attaining of equilibrium data. Silicalite was kindly supplied by Dr. B. Fahlke, Central Institute of Inorganic Chemistry, Academy of Sciences of the GDR. The wet chemical analysis gave no indication of the presence of aluminum or sodium in the sorbent. The crystallinity of the silicalite sample was checked by X-ray diffractometry, sorption capacity measurements, IR spectrometry, and SEM. Prior to application the sorbent was activated in high vacuum ($<10^{-3}$ Pa) for 24 h at 673 K. The hydrocarbons sorbed were gas chromatographically pure.

Results and Discussion

In Figure 1 the calorimetrically determined differential molar heats of sorption for benzene on silicalite are given together with sorption enthalpies derived from isochoric measurements by Pope.[7] Both heat curves have two common features: the constancy of the heats of sorption up to $a \sim 1$ molecule per $^1/_4$ unit cell (uc)

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