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# Tungsten Disulfide: A Novel Hydrogen Evolution Catalyst for Water Decomposition

**Andrzej Sobczynski,[†] Attila Yildiz,[‡] Allen J. Bard, Alan Campion, Marye Anne Fox, Thomas Mallouk, Stephen E. Webber, and John M. White***

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Silica-supported tungsten disulfide was prepared by the reaction of $WO_3/SiO_2$ with $H_2S$ at 300 °C. The $WS_2$ hexagonal structure was confirmed by X-ray diffraction analysis. AES and XPS studies show the existence of residual tungsten oxides in addition to $WS_2$. Hydrogen evolution properties of $WS_2/SiO_2$ were determined by catalytic and photocatalytic (in the presence of fluorescein or CdS as sensitizers) tests and by electrochemical measurements. These were compared with silica-supported platinum. Although a graphite electrode immersed in a $Pt/SiO_2$ slurry evolved hydrogen at a more positive applied potential than in a $WS_2/SiO_2$ slurry, silica-supported tungsten disulfide was more active and stable than $Pt/SiO_2$ for catalytic hydrogen production both in the dark and under visible light illumination (with cadmium sulfide as a sensitizer).

## Introduction

Tungsten disulfide has been widely studied as a catalyst in dehydrogenation and hydrodesulfurization of organic compounds.[1–22] Both unsupported[6–8,14–20] and silica- or alumina-supported $WS_2$[6,7,12–14,20–22] have been prepared. Promotion of $WS_2$ with cobalt and nickel sulfides enhances its catalytic properties by formation of additional active centers.[3,5,6,8,10,12–14,17,18,20–22] The physicochemical properties of tungsten disulfide have also been studied in parallel with its catalytic activity by using various techniques, such as differential thermal analysis,[2] electron microscopy,[13,19,20,22] Mössbauer spectroscopy,[22] surface area and pore size distribution measurements,[4,5,15,19] temperature-programmed reduction,[18,19] electron spin resonance,[2,4,7,10,17,19] X-ray diffraction analysis and related techniques,[2,18,21,22] and X-ray photoelectron spectroscopy.[14,21,22]

Owing to its lamellar structure, which is similar to that of graphite, $WS_2$ has found application in gas chromatography as a specific adsorbent especially for polar organic molecules.[23] In another area, hydrogen evolution on $WS_2$ has been studied by Tseung et al.[24] in a program to develop new methods of preventing sulfide stress corrosion cracking in steel.

The electrochemical and photoelectrochemical properties of both n- and p-type $WS_2$ single crystals have been subjects of extensive investigations.[25–31] The valence and conduction bands[29,30] and flat-band potentials[27,31] for n- and p-$WS_2$ have been determined. Direct and indirect bandgaps are at 1.7 and 1.3 eV, respectively.[26,29,30] Tungsten disulfide is corrosion resistant in concentrated electrolyte solutions, even in strongly acidic media.[25,30] About 7% quantum efficiency has been found for p-type $WS_2$-based photoelectrochemical cells both for conversion of visible light into electricity and for hydrogen evolution from 6 M $H_2SO_4$.[27] Also, n-$WS_2$-based photoelectrochemical cells showed 7.4% efficiency in oxidation of $Cl^-$ and $Br^-$ ions.[28]

The hydrogen evolution properties and corrosion resistance make $WS_2$ a good candidate as an active component of a catalyst for hydrogen photoproduction via photocatalytic decomposition of water. Reported first by Serpone et al.[32–34] and developed further by us,[35] a particulate $CdS/SiO_2$–$Pt/TiO_2/SiO_2$ system for hydrogen production from water in the presence of a sacrificial electron donor makes it easy to study materials other than noble metals as hydrogen evolution catalysts. The advantage of such a system is that separate supported catalyst particles do not interact with the photoactive material (e.g., CdS) during preparation and therefore do not alter its photoelectrochemical properties. Separate particles are particularly relevant in the work reported here because the deposition of tungsten disulfide onto cadmium sulfide particles is impossible under the typical conditions necessary for $WS_2$ preparation (see below). Separately prepared $WS_2$ and CdS particles make the experiment possible.

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Silica-supported tungsten disulfide, prepared by the reaction of $WO_3/SiO_2$ with $H_2S$ at 300 °C, was inactive as a photocatalyst for water splitting in the presence of a sacrificial electron donor. However, its catalytic properties in hydrogen evolution in the presence of a sensitizer were observed, and they are the subject of this paper.

## Experimental Section

*A. Sample Preparation.* Chemicals used in the preparation were all analytical grade.

*$CdS/SiO_2$.* Silica (Cab-O-Sil, EH-5)-supported cadmium sulfide was prepared in the same way as reported earlier[35] and was annealed at 400 °C in argon for 3 h. The final product, $CdS/SiO_2$, contained 16.7% CdS as measured by atomic absorption spectroscopy after dissolution in HCl. It had a specific surface area of 260 $m^2\ g^{-1}$ and contained hexagonal CdS (by XRD).[35]

*$WS_2/SiO_2$.* First, $WO_3/SiO_2$ was prepared in the manner reported previously.[35] After drying and annealing in air at 400 °C, this material was heated in a stream of $H_2S$ at 300 °C for 2–3 h. The resulting $WS_2/SiO_2$ was cooled in argon and stored in air.

*$Pt/SiO_2$.* A 1 wt % sample of Pt on silica was prepared by impregnation of $SiO_2$ with an appropriate amount of $H_2PtCl_6$ solution followed by calcination under oxygen at 400 °C for 1 h and reduction in hydrogen at 400 °C for 1 h.

*B. Sample Characterization.* BET specific surface areas were measured by nitrogen adsorption at 77 K using a surface area analyzer (Micromeritics, Model 220-00000-00).

XRD measurements were performed on a Phillips automated powder diffractometer using Cu K$\alpha$ radiation.

XPS and AES spectra of $WS_2/SiO_2$ and, for comparison purposes, of commercial $WS_2$ (Johnson Matthey Co.) were taken on a VG ESCALAB spectrometer with Mg K$\alpha$ radiation. The measurements were performed both before and after outgassing the samples under vacuum at 300 °C.

*C. Electrochemical Measurements.* Two kinds of systems were used: (1) a titanium metal electrode with a $WS_2$ film on it and (2) a graphite electrode immersed in a slurry of the hydrogen evolution catalyst. $WS_2/Ti$ electrodes were prepared by painting freshly precipitated $WO_3$–gel on an etched ($HNO_3$:HF:$H_2O$ = 1:1:50) titanium foil and reducing the resulting tungsten trioxide film in a stream of $H_2S$ at 300 °C for 3 h. A graphite electrode was made of pyrolytic graphite (Union Carbide).

Current–voltage curves were taken on a PAR Model 173 potentiostat–galvanostat coupled with a PAR Model 175 Universal Programmer and Houston Instrument Model 2000 *X–Y* recorder. The electrolyte was 0.5 M KCl solution. The solution included the slurry of $WS_2/SiO_2$ or $Pt/SiO_2$ when graphite electrodes were used.

*D. Dark Catalytic Hydrogen Evolution from $V^{2+}$ Solution.* A 0.5 M $VCl_3$ solution in 30% $H_2SO_4$ was prepared, and vanadium(III) ions were reduced to V(II) by zinc amalgam. The reduction and storage were done under argon. Twenty milliliters of water was poured into a reaction cell (approximate volume 40 mL) and deaerated in flowing argon. Ten milliliters of the above $V^{2+}$ solution was injected through the septum into the reaction cell. The catalyst ($WS_2/SiO_2$ or $Pt/SiO_2$) slurry in water was prepared by sonication of 10 mg of the appropriate powder in 10 mL of water under flowing argon. Then 0.2 mL of this deaerated catalyst slurry was injected into the reaction cell. The cell was kept in the dark, and the reaction mixture was stirred with magnetic stirrer (small, Pyrex-covered stir bar). The hydrogen evolved was analyzed by GC.[35]

*E. Hydrogen Photoevolution in the Presence of $3.3 \times 10^{-4}$ M Fluorescein and EDTA.* A 10-mg sample of $WS_2/SiO_2$ or $Pt/SiO_2$ was placed in a reaction cell. Five milliliters of $2 \times 10^{-3}$ M aqueous fluorescein solution, 0.1117 g of EDTA (the resulting EDTA concentration was $1 \times 10^{-2}$ M), and 25 mL of water were added. The cell was deaerated, irradiated with a 1000-W Xe lamp (equipped with a 420- or 435-nm cutoff filter and water jacket to remove IR), and analyzed for hydrogen formation.

*F. Hydrogen Photoproduction with a Mixture of $CdS/SiO_2$ and $WS_2/SiO_2$ or $Pt/SiO_2$ and Methanol as a Sacrificial Electron Donor.* In most experiments 10 mg of $CdS/SiO_2$ and 10 mg of $WS_2/SiO_2$ (or $Pt/SiO_2$) were mixed with 15 mL of methanol, 12 mL of water, and 3 mL of 1.0 M KOH in a Pyrex reaction cell (40-mL volume). The cell was closed with a septum and was deaerated under flowing argon by using two needles that penetrated the septum. After the cell had been deaerated (no air contamination by GC) it was irradiated with a 1000-W Xe lamp (435-nm cutoff filter and water jacket) while the mixture was stirred with a magnetic stirrer. The hydrogen produced was analyzed by GC.

The lower limit for the quantum efficiency of hydrogen photogeneration on $CdS/SiO_2$–$WS_2/SiO_2$ was measured under illumination of a 200-W high-pressure Hg lamp equipped with a 420-nm cutoff filter. The light flux was measured with an uranyl oxalate actinometer.[35]

## Results and Discussion

Characterization of $CdS/SiO_2$ powder has been described in our previous paper.[35] The powder contains 16.7 wt % CdS which is equivalent to $3.8 \times 10^{18}$ CdS molecules per 1 $m^2$ of the catalyst.

$WS_2/SiO_2$ prepared by the reaction of $WO_3/SiO_2$ with $H_2S$ at 300 °C was black and had a specific surface area of 160 $m^2\ g^{-1}$. It contains 22.5 wt % $WS_2$ supported on silica, which is equivalent to $3.4 \times 10^{18}$ $WS_2$ molecules per 1 $m^2$ of the powder. By XRD, the $WS_2$ supported on silica was hexagonal[36] with the positions of the powder diffraction lines identical with those of commercial $WS_2$ (Johnson Matthey Co.). There was no evidence for any other crystalline phase of $WS_2$.

XPS and AES measurements confirm the existence of tungsten disulfide. For both commercial and silica-supported $WS_2$, W $4f_{7/2}$ peaks with binding energies between 31 and 36 eV and sulfur 2p peaks with a binding energy of about 162 eV were found. Commercial $WS_2$ showed an oxygen 2s peak with a maximum at 531 eV; the peak disappeared after outgassing under vacuum at 300 °C. Silica-supported tungsten disulfide showed two O(2s) peaks: at 531 and 538 eV. The latter is identical with that measured for the silica support and indicates that the silica surface was only partly covered by tungsten disulfide. The high binding energy reflects differential surface charging of parts of the sample. The 531-eV peak did not disappear after outgassing under vacuum at 300 °C. Therefore, it cannot be attributed to water molecules adsorbed on $WS_2/SiO_2$ surface. We conclude that silica-supported $WS_2$ includes small amounts of $O^{2-}$ ions which originate from the original $WO_3$. Thus, although most of the $WO_3$ was converted to $WS_2$, the reaction did not reach completion.

Two different experiments were performed to establish the hydrogen evolution properties of silica-supported $WS_2$ and, for comparison purposes, of $Pt/SiO_2$: (1) dark catalytic hydrogen evolution from acidic $V^{2+}$ solution (1 M $H_2SO_4$) and (2) hydrogen production via illumination of fluorescein (sensitizer) solution in the presence of a sacrificial electron donor at pH 5.

Highly dispersed noble metals have been used by many authors as catalysts for hydrogen evolution from water, both in the presence of a strong reducing agent (e.g., $V^{2+}$, $Cr^{2+}$, $MV^+$)[37–39] and in the presence of various excited sensitizers.[40–42] The theory of electron transfer from a reductor or an excited dye molecule to the metal "microelectrode" has been derived and confirmed experimentally.[37,38] Similarly, electron injection from an excited sensitizer

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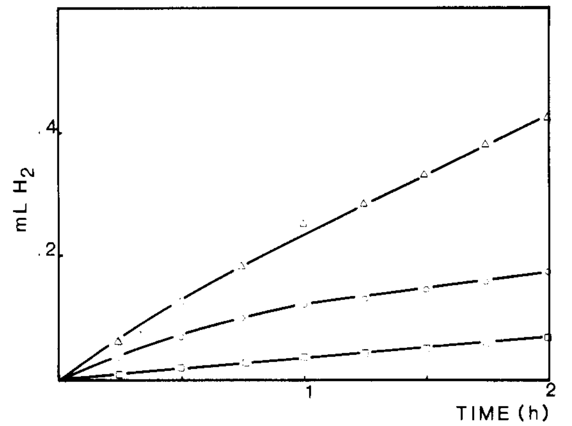

**Figure 1.** Dark catalytic hydrogen evolution from acidic $V^{2+}$ solution (1 M $H_2SO_4$): (△) $WS_2/SiO_2$, (○) $Pt/SiO_2$, (□) without catalyst.

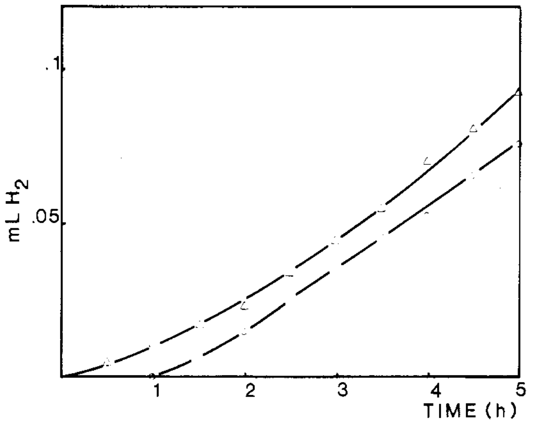

**Figure 2.** Hydrogen photoevolution from $3.3 \times 10^{-4}$ M fluorescein and $1 \times 10^{-2}$ M EDTA solution: (○) $WS_2/SiO_2$, (△) $Pt/SiO_2$.

molecule into colloidal semiconductors has been observed and a mechanism of electron transfer has been proposed.[43]

The results of dark hydrogen evolution from 0.16 M $V^{2+}$ solution in 1 M $H_2SO_4$ are shown in Figure 1. The activity of silica-supported tungsten disulfide is very high: the hydrogen production rate exceeds 0.2 mL $h^{-1}$ per 0.2 mg of the catalyst. The rate decreases only a little with time over 2 h. $Pt/SiO_2$ evolved about 0.1 mL of $H_2$ during the first hour but only 0.04 mL of $H_2$ in the second hour. A blank test showed that very small amounts of hydrogen (0.015 mL $h^{-1}$) were evolved in the absence of any catalyst. The addition of 0.2 mg of $TiO_2/SiO_2$ did not alter the rate of $H_2$ production observed in the blank experiment. Similarly, illumination of a $WS_2/SiO_2$ slurry ($\lambda > 435$ nm) in $V^{2+}$–1 M $H_2SO_4$ solution had no influence on the dark hydrogen production rate.

Both $WS_2/SiO_2$ and $Pt/SiO_2$ show hydrogen evolution activity in experiments with illuminated ($\lambda > 420$ nm) fluorescein in the presence of $1 \times 10^{-2}$ M EDTA as a sacrificial electron donor (Figure 2). Hydrogen evolution on $WS_2/SiO_2$ shows a long induction period (about 1 h). The lack of hydrogen in the early stages of illumination is also observed with a $WS_2/SiO_2$–$CdS/SiO_2$ slurry in water–methanol–KOH and is discussed below.

Although single-crystal $WS_2$ electrodes give reasonably high photocurrents under visible irradiation and show reasonable stability, especially in acidic media,[25-31] our $WS_2/SiO_2$ powders show no photoresponse. Therefore, $WS_2$ films on titanium electrodes were prepared and current–voltage measurements were performed in 0.5 M KCl both in the dark and under illumination with visible light ($\lambda > 435$ nm). In the dark neither cathodic nor anodic currents (hydrogen and oxygen evolution currents) were observed unless some of the $WS_2$ film came off, leaving parts of the conductive $TiO_2$ electrode exposed. These evolve hydrogen from 0.5 M KCl, at an applied potential about 0.4 V less negative than a naked Ti electrode (–0.9 and –1.3 V vs SCE, respectively). There was no photoresponse.

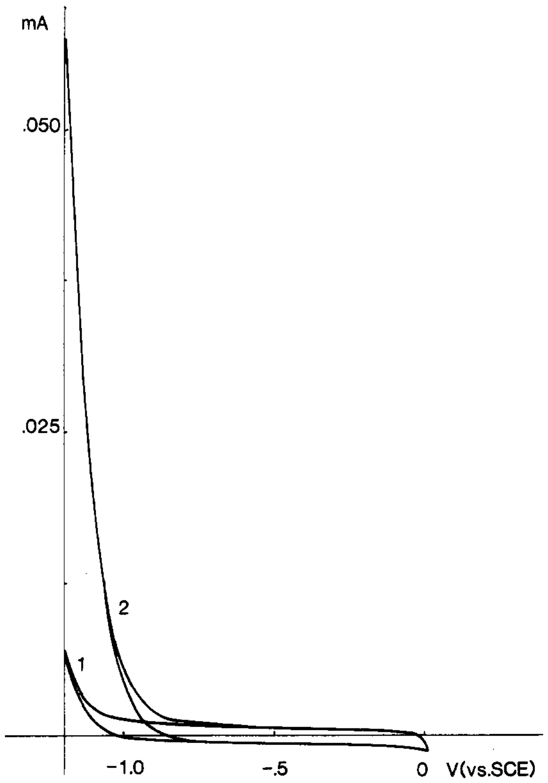

**Figure 3.** Dark current vs applied voltage for graphite electrode in (1) 0.5 M KCl and (2) $WS_2/SiO_2$ (15 mg) slurry in 0.5 M KCl.

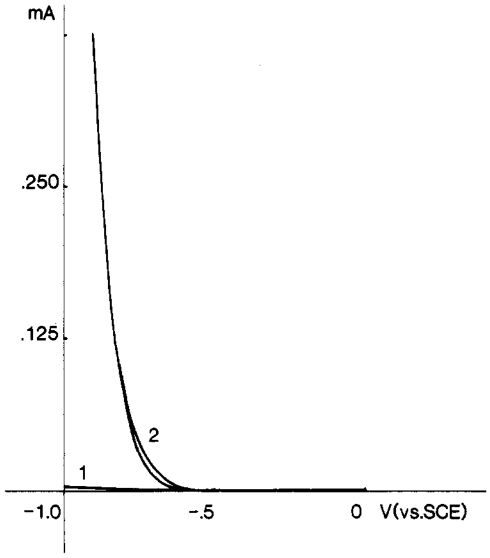

**Figure 4.** Dark current vs applied voltage for graphite electrode in (1) 0.5 M KCl and (2) $Pt/SiO_2$ (15 mg) slurry in 0.5 M KCl.

A positive shift of the potential required for hydrogen evolution from the pyrolytic graphite electrode was observed when $WS_2/SiO_2$ powder was added to 0.5 M KCl (see Figure 3). For comparison, similar current–voltage measurements were performed with graphite electrodes immersed in the $Pt/SiO_2$ slurry in 0.5 M KCl (Figure 4). It is obvious that the effect of platinum (which

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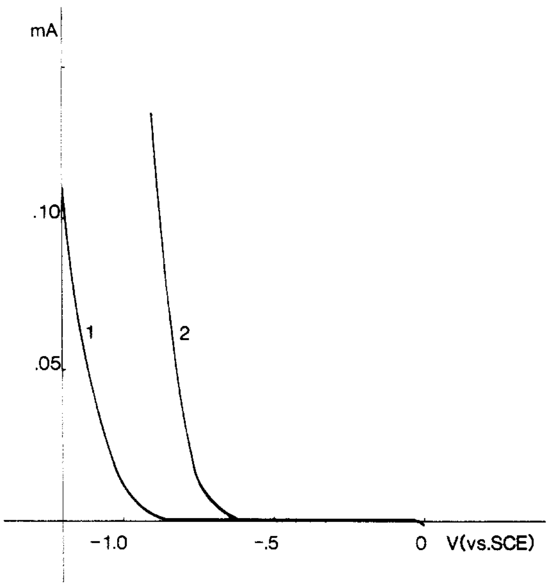

**Figure 5.** Dark current vs applied voltage in 0.5 M KCl for graphite electrodes which were immersed previously in (1) $WS_2/SiO_2$ slurry in 0.5 M KCl and (2) $Pt/SiO_2$ slurry in 0.5 M KCl and subsequently sonicated in pure solvents (see text).

possesses a low overpotential for hydrogen evolution) on the performance of a graphite electrode is stronger than that of tungsten disulfide. The observed cathodic currents, in both $WS_2/SiO_2$ and $Pt/SiO_2$ slurries, increased with time and catalyst concentration, indicating that the catalyst was incorporated into the electrode structure. This was confirmed in the following experiments: after *I–V* measurements in $WS_2/SiO_2$ or $Pt/SiO_2$ slurries the graphite electrodes were washed and sonicated in acetone and water, and *I–V* curves were taken again in 0.5 M potassium chloride. Both electrodes showed positive shifts of hydrogen evolution potentials like those observed in the experiments with catalyst slurries (Figure 5).

The addition of 5 mg of $WS_2/SiO_2$ (the largest amount of powder added) to 0.5 M KCl solution changes the pH from 5.85 to 4.85. This shifts the redox potential of the $H^+/H_2O$ couple by +0.059 V, which is small compared to the shift caused by tungsten disulfide ($\approx$0.3 V). These results confirm the catalytic properties of tungsten disulfide for hydrogen evolution.

As noted above, interparticle electron transfer is effective in hydrogen production by water splitting in the presence of illuminated cadmium sulfide.[32-35] Therefore, we studied hydrogen photoevolution ($\lambda > 435$ nm) using the system $CdS/SiO_2$–$WS_2/SiO_2$ and, for comparison, $CdS/SiO_2$–$Pt/SiO_2$. In both cases *separate* silica particles support the two key components. First, we establish the influence of KOH concentration on hydrogen production rate from water–methanol–KOH solution. The rate increased with KOH concentration in the range 0–0.1 M. Higher concentrations lead to corrosion and were not investigated. Therefore 0.1 M KOH was used as a standard. Importantly, $WS_2/SiO_2$ alone did not produce hydrogen from water–methanol–0.1 M KOH when irradiated with $\lambda > 435$ nm.

Hydrogen evolution from water–methanol–0.1 M KOH with $CdS/SiO_2$–$WS_2/SiO_2$ shows a long induction period (1–2 h), after which the rate remains nearly constant. The results shown in Figures 6 and 7 were obtained after the slurry had been first irradiated for 2 h and outgassed again in a stream of argon. Clearly, the long induction period is not repeated as the hydrogen evolution rates are nearly constant from the beginning of the second illumination period. Among the three $WS_2/SiO_2$ samples which differ slightly in preparation, the most active sample is prepared from $WO_3/SiO_2$ annealed 2 h in air at 400 °C and then reduced in hydrogen sulfide at 300 °C for 2 h. This $WS_2/SiO_2$ sample was used in subsequent experiments. Figure 7 shows hydrogen evolution rates obtained by using different amounts of catalysts. Equivalent amounts of $WS_2/SiO_2$ and $CdS/SiO_2$ (10 mg of each) give reasonable hydrogen production. A twofold increase in $CdS/SiO_2$ gave an increase of less than 20%, whereas a twofold increase in $WS_2/SiO_2$ concentration decreased the hydrogen production rate. The latter is presumably due to enhanced light scattering on $WS_2/SiO_2$ particles.

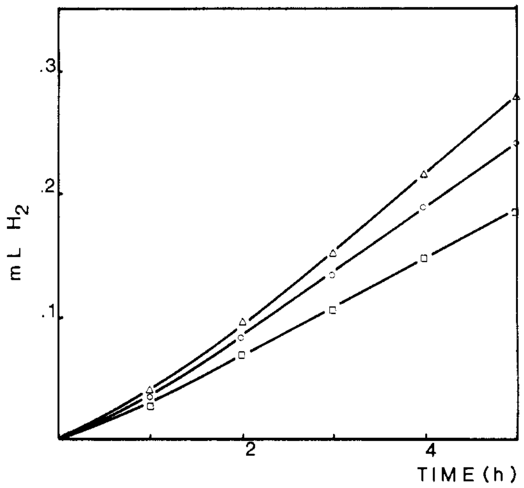

**Figure 6.** Hydrogen evolution from water–methanol–KOH with different $WS_2/SiO_2$ powders: (△) $WO_3/SiO_2$ annealed at 400 °C in air for 3 h, reaction with $H_2S$ at 300 °C for 2 h; (○) $WO_3/SiO_2$ annealed at 400 °C in air for 3 h, reaction with $H_2S$ at 300 °C for 3 h; (□) $WO_3/SiO_2$ dried at 110 °C, reaction with $H_2S$ at 300 °C for 3 h. Note: the slurries were preirradiated with $\lambda > 435$ nm for 2 h and hydrogen was removed by flushing with argon.

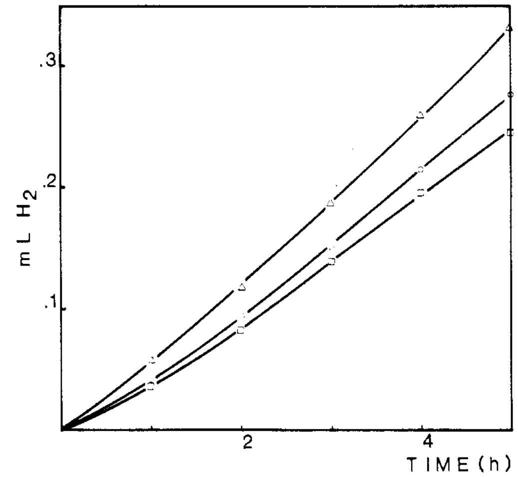

**Figure 7.** Hydrogen evolution from water–methanol–KOH with different amounts of catalysts: (△) 20 mg of $CdS/SiO_2$–10 mg of $WS_2/SiO_2$, (○) 10 mg of $CdS/SiO_2$–10 mg of $WS_2/SiO_2$, (□) 10 mg of $CdS/SiO_2$–20 mg of $WS_2/SiO_2$. See note in caption to Figure 6.

In a long-term experiment with 10 mg of $CdS/SiO_2$ and 10 mg of $WS_2/SiO_2$ (7 days of illumination), the hydrogen evolution rate was 0.06 mL $h^{-1}$ and did not change with time. The turnover number, defined as a ratio of moles of $H_2$ produced to moles of $WS_2$, was 41 after 7 days of irradiation.

In a separate experiment using a high-pressure Hg lamp equipped with 420-nm cutoff filter we established a lower limit for the quantum yield (by calculating the ratio of twice the moles of $H_2$ evolved to moles of quanta ($400 < \lambda < 500$ nm) which entered the cell). The result was 1.7% for the $CdS/SiO_2$–$WS_2/SiO_2$ system. This is 30% higher than that observed previously for $CdS/SiO_2$–$Pt/TiO_2/SiO_2$ slurry in water–methanol–KOH.[35]

We now turn to the induction period. Figure 8 shows hydrogen evolution *rates* (not total yield) on $WS_2/SiO_2$–$CdS/SiO_2$ and, for comparison, on $Pt/SiO_2$·$CdS/SiO_2$ for the first few hours of visible light illumination. When a platinum catalyst is used, there is no induction period and the rate decays with time. On the contrary, for $WS_2$ a long induction period (zero or increasing rate) is observed. In our opinion, the low rate of hydrogen production

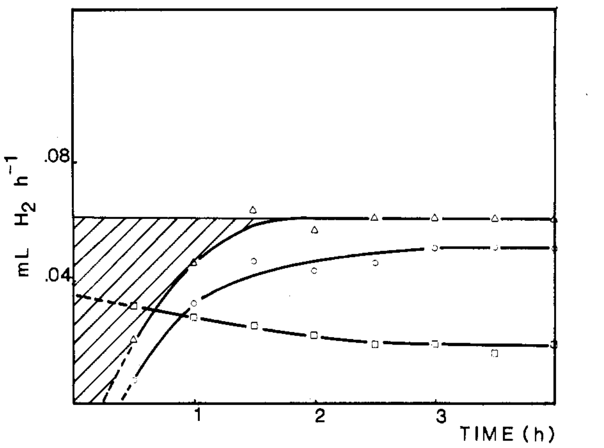

**Figure 8.** Hydrogen evolution rates vs time in water–methanol–KOH on (○) 10 mg of $CdS/SiO_2$–10 mg of $WS_2/SiO_2$, (△) 10 mg of $CdS/SiO_2$–20 mg of $WS_2/SiO_2$, and (□) 10 mg of $CdS/SiO_2$–10 mg of $Pt/SiO_2$. According to the model described in the text, the cross-hatched area is the amount of hydrogen taken by the catalyst during the induction period.

at the early stage of irradiation is due to consumption of $H_2$ by $WS_2/SiO_2$. If we assume that the total rate is constant from the beginning of the irradiation, we can calculate the quantity of hydrogen consumed (i.e., the area of the hatched region of Figure 8). By this method, 10 mg of $WS_2/SiO_2$ consumes 0.02 mL of $H_2$ while 20 mg of $WS_2/SiO_2$ consumes nearly twice as much (0.038 mL). Thus, it is reasonable to conclude that the induction period is proportional to the amount of $WS_2$ and involves hydrogen consumption. This is supported by the observation noted above, that the induction period is not repeated when fresh solutions are tested with a catalyst that has passed through the induction period.

There are at least two possible explanations involving hydrogen consumption leading to an induction time: (1) adsorption of hydrogen on the surface and within the layers of tungsten disulfide and (2) the reaction of atomic hydrogen, produced by electrons in the conduction band of excited CdS with surface $W^{4+}$ ions which results both in tungsten(IV) reduction and in the transfer of $S^{2-}$ ions from the catalyst surface to the solution. From literature data, both adsorption of hydrogen[44] and reduction of $W^{4+}$ [18,19] on the surface are possible. A simple test using a solution of lead acetate in 1 M KOH showed that, after illumination of a $WS_2/SiO_2$–$CdS/SiO_2$ suspension, the filtered solution contained $S^{2-}$ ions. No $S^{2-}$ was found after irradiation of $Pt/SiO_2$–$CdS/SiO_2$ in water–methanol–KOH. This shows that $S^{2-}$ ions originate from $WS_2$. Only very small amounts of $S^{2-}$ (quantitative analysis has not been performed) were found in water–methanol–KOH solution which contained only $WS_2/SiO_2$ and was kept in dark. That the amount of hydrogen consumed is proportional to the total amount of $WS_2$ used suggests that more than the outermost surface species are involved.

## Summary

High surface area tungsten disulfide has been prepared by deposition on a silica support. Hexagonal $WS_2$ was confirmed by XRD. AES and XPS studies indicated that $WS_2$ included small amounts of $O^{2-}$ ions which originated from the original $WO_3$. The electrochemical studies showed that, although silica-supported tungsten disulfide did not manifest any photoresponse, it possessed good hydrogen evolution properties. These properties were confirmed both in catalytic studies, in the presence of $V^{2+}$ in 1 M $H_2SO_4$, and in photocatalytic studies in the presence of fluorescein or CdS as sensitizers and organic molecules as sacrificial electron donors. Compared to $Pt/SiO_2$, $WS_2/SiO_2$ showed better hydrogen evolution activity and stability in a solution of $V^{2+}$ in 1 M $H_2SO_4$ and in an irradiated slurry of $CdS/SiO_2$ in water–methanol–0.1 M KOH. The activity of the particulate $WS_2/SiO_2$–$CdS/SiO_2$ system in water–methanol–0.1 M KOH was stable during 7 days of visible light illumination. The long induction period in hydrogen evolution observed with $WS_2/SiO_2$ can be connected to hydrogen adsorption by $WS_2$ and/or to the reaction of atomic hydrogen with surface $W^{4+}$ ions.

*Acknowledgment.* We thank Dr. Tuo Jin for obtaining XPS and AES spectra. This work was supported in part by the Gas Research Institute.

**Registry No.** $WS_2$, 12138-09-9; $SiO_2$, 7631-86-9; $WO_3$, 1314-35-8; $V^{2+}$, 15121-26-3; CdS, 1306-23-6; $H_2$, 1333-74-0; $H_2O$, 7732-18-5; fluorescein, 2321-07-5; methanol, 67-56-1.

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(44) Fraser, D.; Moyes, R. B.; Wells, P. B. *Stud. Surf. Sci. Catal.* **1981**, *7*, 1424.