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J. Phys. Chem., **1987**, 91 (12), 3316-3320 • DOI: 10.1021/j100296a041

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Photoassisted Hydrogen Generation: Pt and CdS Supported on Separate Particles

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(Received: December 22, 1986)

The visible light photoassisted production of hydrogen from methanol-water solutions containing mixtures of small particles of CdS/SiO₂ and a platinized wide-band-gap semiconductor (TiO₂, ZnO, SnO₂, or WO₃) separately supported on silica was studied. The activity is higher for these separately supported particles than for samples prepared by depositing the active materials together on the silica particles. The efficiency of hydrogen production is not dependent on the energy of the conduction band of the wide-band-gap metal oxide. Hence, we conclude that electron injection from the conduction band of CdS into the conduction band of the metal oxide is not an important pathway for charge transport to the Pt particles. These oxides do improve the hydrogen production activity of the platinum formed during photoplatinization. CdS/SiO₂ particles attach to pellets of the platinized oxide and we propose on this basis that agglomeration of the separate oxide- and sulfide-containing particles is important for photoassisted hydrogen production.

1. Introduction

Many different semiconducting materials have been used as photocatalysts for hydrogen generation from water. Among them platinized titania shows the best activity and stability during irradiation both in acidic and basic media.¹⁻³ However, the disadvantage of this material is its wide band gap, which requires the use of near-UV light to excite electrons to the conduction band. On the other hand, the band gap of CdS (2.4 eV) corresponds well with the spectrum of sunlight, but its stability is much worse.⁴⁻⁷ Serpone et al. found an improvement of the efficiency of hydrogen generation on irradiated CdS particles in water solutions containing Na₂S or methanol as sacrificial reagents upon deposition of a redox catalyst (Pt or RuO₂) on separate TiO₂^{8,9} or Al₂O₃¹⁰ particles. The authors ascribe this effect to a more efficient charge separation caused by an interparticle electron transfer from the conduction band of an excited CdS either to the conduction band of TiO₂ or directly to the redox catalyst.

The distribution of platinum plays a crucial role in hydrogen evolution on irradiated semiconductors.¹¹ Many methods of platinum (or other noble metal) deposition on semiconductors have been developed.¹²⁻²⁴ Photoplatinization¹⁶⁻²⁰ utilizing the photo-produced electrons in the conduction band (CB) of the semiconductor support offers the possibility of controlling the morphology of the supported metal by simple alteration of the reaction conditions for deposition.¹¹

Whether the CB of the wide-band-gap semiconductor (e.g. TiO₂) mediates interparticle electron transfer from the CB of an excited CdS particle to a Pt particle separately supported on the TiO₂ (or other wide-gap oxide) has not been established. The conduction band of anatase is slightly more negative than the redox potential of H₃O⁺/H₂ couple and platinized titania evolves hydrogen from water (in the presence of a sacrificial donor) when irradiated with a light of energy equal to or higher than its band gap.²⁵ Because of the position of its conduction band, electrons can be supplied by the excited cadmium sulfide to the CB of TiO₂ and there have energies sufficient to reduce H₃O⁺. The mechanism of hydrogen evolution involving interparticle electron transfer mediate by the CB of titania is shown schematically in Figure 1A. The alternative mechanism, in which the electrons are transferred directly from the CB of CdS to the supported platinum, is shown in Figure 1B.

To establish the role of the wide-band-gap semiconductor, platinum was deposited on TiO₂, ZnO, SnO₂, and WO₃. The oxides were themselves dispersed on a high-surface-area amorphous silica. In this way the specific surface areas of the samples were similar.

ZnO, SnO₂, and WO₃ were chosen since their conduction band edges were more positive than the redox potential of the H₃O⁺/H₂ couple (see Figure 4). It was verified that they did not evolve hydrogen from a water-methanol mixture under band-gap irradiation. Therefore, if interparticle electron transfer from the CB of CdS to Pt involves intermediate population of the CB of the metal oxide, hydrogen should not evolve.

Our results demonstrate that the activity of physically mixed CdS/SiO₂ and Pt/ZnO(or SnO₂, WO₃)/SiO₂ in water-methanol under visible light irradiation is similar to that of CdS/SiO₂ mixed with Pt/TiO₂/SiO₂. This observation excludes the participation of the CB of the wide-band-gap semiconductor in the interparticle electron transfer (Figure 1A) and favors direct electron transfer from the CB of CdS to the separately supported platinum (Figure 1B). We also demonstrate identical activity of platinum supported

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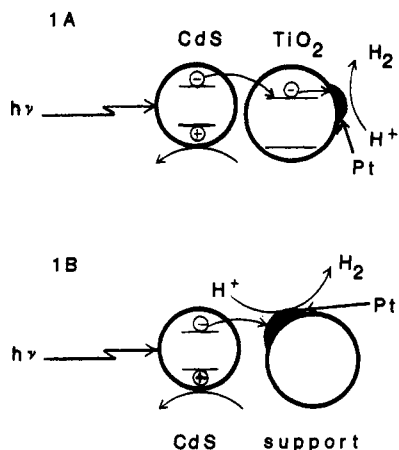


Figure 1. Interparticle electron transfer: (A) mediated by the conduction band of TiO_2 ; (B) direct electron transfer to separately supported platinum.

on SiO_2 and $\text{TiO}_2/\text{SiO}_2$ (using an impregnation method). Photoplatinization of TiO_2 and the other wide-band-gap semiconductors gives well-dispersed platinum, which in turn enhances its catalytic efficiency. The agglomeration of the particles of CdS/SiO_2 and of separately supported platinum is proposed to account for the relatively efficient charge transfer.

2. Experimental Section

2.1. Sample Preparation. The chemicals used for sample preparation were all analytical grade.

CdS/SiO_2 . Ten grams of fumed silica (amorphous, Cab-O-Sil, EH-5) was stirred overnight with 4 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fischer Co.) in 500 mL of water. Then 2.762 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added. After the solution was stirred for 6 h, several drops of concentrated HNO_3 were added to adjust the solution to pH 4. This mixture containing CdS/SiO_2 was stirred for 24 h, filtered, and washed with water. After drying overnight, the product was split into two fractions, one of which was annealed under argon for 4 h, at 300 °C and the other at 400 °C. The samples are designated as $\text{CdS}/\text{SiO}_2(300)$ and $\text{CdS}/\text{SiO}_2(400)$, respectively.

$\text{TiO}_2/\text{SiO}_2$. Ten milliliter of TiCl_3 solution (Alpha Products) containing 2.43×10^{-3} mol of Ti^{3+} mL^{-1} (based on gravimetric analysis of TiO_2 precipitated from the solution) was added to 10.52 g of SiO_2 (Cab-O-Sil, EH-5) and 500 mL of water. The slurry was stirred overnight and then heated to 80 °C, and the hydroxide of titanium was precipitated by raising the pH to 8 with aqueous ammonia. The $\text{Ti}(\text{OH})_3/\text{SiO}_2$ was filtered and washed with water to remove Cl^- . Then 500 mL of water was added, the temperature was raised to 80 °C, and O_2 was bubbled in to oxidize $\text{Ti}(\text{III})$ to $\text{Ti}(\text{IV})$. The product was filtered and dried in air at 110 °C to give a sample denoted ($\text{TiO}_2/\text{SiO}_2(110)$) portions of which were annealed at 300 or 400 °C in air for 4 h giving $\text{TiO}_2/\text{SiO}_2(300)$ and $\text{TiO}_2/\text{SiO}_2(400)$, respectively.

ZnO/SiO_2 . A mixture of 1.5 g of SiO_2 and 0.235 g of ZnCl_2 in 200 mL of water was stirred overnight, acidified with 1 drop of concentrated HCl , and mixed with 25 mL of a solution of 0.4 g of $\text{Na}_2\text{C}_2\text{O}_4$ in 2 M NH_3 to precipitate zinc oxalate. The suspension was heated at 70 °C for 1 h. The precipitate was filtered, washed with water, and dried overnight at 110 °C. The resulting $\text{ZnC}_2\text{O}_4/\text{SiO}_2$ was heated in air at 400 °C for 4 h.

$\text{SnO}_2/\text{SiO}_2$. Concentrated HCl was added to a suspension of 0.3892 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 1.5 g of SiO_2 to dissolve the black precipitate of tin chloride. The slurry was stirred overnight, heated to 70 °C, and mixed with concentrated Na_2CO_3 to raise the pH to 9. The precipitate was filtered, washed with water, and dried overnight at 110 °C. The dry precipitate was annealed at 400 °C in air for 4 h.

WO_3/SiO_2 . A suspension of 1.5 g of SiO_2 and 0.5690 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in 30 mL of water was stirred overnight and then was poured into 75 mL of boiling, concentrated HCl . The resulting pale yellow slurry was stirred for 1 h, filtered, washed with a 5% solution of aqueous NH_4NO_3 , and dried at 110 °C. Then the dry

powder was annealed at 400 °C in air 4 h.

All the samples were stored in closed vials in air at room temperature.

2.2. Sample Characterization. BET specific surface area measurements were performed on a surface area analyzer (Micromeritics, Model 220-00000-00) using N_2 adsorption at 77 K.

XRD spectra were taken on a Phillips automated powder diffractometer using $\text{Cu K}\alpha$ irradiation.

2.3. Hydrogen Photoevolution Experiments. In most experiments platinum was deposited on the particles of $\text{TiO}_2/\text{SiO}_2$, ZnO/SiO_2 , $\text{SnO}_2/\text{SiO}_2$, or WO_3/SiO_2 by photoplatinization of a solution containing H_2PtCl_6 . The catalyst was placed in a Pyrex reaction cell and an appropriate amount of H_2PtCl_6 (0.002 g of Pt cm^{-3}) and water-methanol (1:1) solutions were added. The resistivity of the water was 18 $\text{M}\Omega \text{ cm}$. The cell was closed with a septum and the slurry was sonicated and deaerated under flowing argon by using two needles that penetrated the septum. On the basis of gas chromatography, there was no detectable contamination by air. After the cell had been deaerated, it was placed in a water bath and platinization proceeded by irradiation with a high-pressure 200-W Hg lamp for 1 h. The silica-supported semiconductor particles were suspended by using a magnetic stirrer. Hydrogen, evolved during illumination, was analyzed gas-chromatographically (13X molecular sieves column, argon carrier gas, and thermal conductivity detector).

After the sample had been platinized, CdS/SiO_2 and KOH solution were added, the cell was sonicated, deaerated again, and illuminated with a 450-W (or, in some experiments, 1000-W) Xe lamp after passage through a glass 435-nm cutoff filter and a water jacket to remove UV and IR. The amount of hydrogen produced was measured after each hour by GC.

Any exceptions to this procedure are specifically noted in the text.

2.4. CdS/SiO_2 Adsorption on $\text{Pt}/\text{TiO}_2/\text{SiO}_2$ Pellets. $\text{TiO}_2/\text{SiO}_2(110)$ (200 mg) was mixed with several drops of water and pressed at 500 psi in a pellet press. Fresh pellets were dried in air at 80 °C and then at 110 °C. Dry pellets were annealed at 400 °C in air for 4 h. The resulting pellets were rectangular with dimensions $25 \times 5 \times 2$ mm. They were mechanically stable in water and methanol, both in acidic and basic solutions.

The surface areas of the pellets were determined by using methylene blue adsorption from aqueous solution.²⁶ Each pellet was soaked overnight in the resulting solution. The loss of the methylene blue in the solution was measured spectrophotometrically ($\lambda = 366$ nm). The surface area of the pellets was about 0.086 m^2 . The dye adsorption surface area for $\text{TiO}_2/\text{SiO}_2$ powder annealed at 400 °C was measured (11.2 $\text{m}^2 \text{ g}^{-1}$). This value was used as discussed in section 3.5 to determine the amount of chloroplatinic acid to use.

Platinum deposition on the pellets was performed as follows: 20 μL of a H_2PtCl_6 solution (containing 0.002 g of Pt cm^{-3}) was added to 3 mL of 1:1 water-methanol. Each pellet was soaked overnight in the resulting solution. The pellets were irradiated with a 200-W high-pressure Hg lamp for 2 h under bubbling argon; they were turned frequently to give uniformly darkened surfaces.

A slurry of 20 mg of $\text{CdS}/\text{SiO}_2(400)$ in water-methanol-0.1 M KOH (12 + 15 + 3 mL) was prepared. For comparison purposes, solutions of the same composition were also used for other hydrogen evolution experiments not involving pellets. Each platinized pellet was immersed in 3 mL of the above solution in a Pyrex vial. Two pellets were kept in the dark for 2 h; two others were irradiated with a 1000-W Xe lamp, equipped with a 435-nm cutoff filter. The pellets were turned occasionally during illumination for even exposure. The pellets were rinsed three times in water-methanol-KOH solutions and then were treated with 2 mL of concentrated HCl for 15 min to dissolve adsorbed CdS . The amount of cadmium was determined by an atomic absorption spectroscopy. The Cd concentration was determined by the same

TABLE I: Hydrogen Evolution from Water–Methanol on Platinized TiO₂/SiO₂ under UV Irradiation^a

catalyst	KOH concn, mol dm ⁻³	Pt, amount, wt %	H ₂ yield, μL h ⁻¹	
			1 h	2 h
TiO ₂ /SiO ₂ (400)	0.01	0.2	130	150
TiO ₂ /SiO ₂ (400)	0.00	0.2	490	400
TiO ₂ /SiO ₂ (400)	0.00	0.4	490	520
TiO ₂ /SiO ₂ (400)	0.00	0.8	460	440
TiO ₂ /SiO ₂ (300)	0.00	0.4	420	210
TiO ₂ /SiO ₂ (110)	0.00	0.4	170	50

^a Reaction conditions: 10 mg of TiO₂/SiO₂; in situ photoplatinization; 10 mL of 1:1 H₂O–MeOH; light source: 200-W Hg lamp; H₂ was removed off the cell after 1 h of irradiation.

procedure in the CdS/SiO₂ powder used in the slurry.

3. Results

3.1. Sample Characterization and Hydrogen Photoevolution on TiO₂/SiO₂. The three TiO₂/SiO₂ samples, annealed at different temperatures (110, 300, and 400 °C) contained 16.5 wt % TiO₂ supported on silica. The specific surface areas of the all samples are the same (about 260 m² g⁻¹), independent of the annealing temperature. The XRD spectra of the samples are identical and show very weak anatase lines whereas the SiO₂ support remains amorphous. There are about 4.5 × 10¹⁸ molecules m⁻², which corresponds approximately to monolayer coverage of the support.³² At such low coverage, the specific surface areas of TiO₂/SiO₂ samples should depend only on SiO₂.

The results of hydrogen photoevolution in methanol–water solutions on platinized TiO₂/SiO₂ obtained using UV irradiation are collected in Table I. All experiments involve in situ photoplatinization of the wide-band-gap oxide. The following points are derived from the data of the Table I.

1. The rate of hydrogen photoevolution without KOH is much higher than with KOH (0.01 M solution). Thus, photoplatinization of TiO₂/SiO₂ in aqueous methanol in the absence of KOH produces a much better catalyst and this method of metal deposition was used for further studies reported below.

2. The optimum Pt content is 0.4 wt %. This optimum platinum coverage was used in all further experiments.

3. The most active and stable catalyst during UV illumination is TiO₂/SiO₂ annealed at 400 °C.

4. The specific hydrogen evolution rate is about 0.3 mL of H₂ per mg of TiO₂ for the most active sample.

3.2. Sample Characterization and Hydrogen Photoevolution on CdS/SiO₂. CdS/SiO₂ samples, annealed at 110, 300, and 400 °C, contain 16.7 wt % CdS, which is equivalent to 3.8 × 10¹⁸ CdS molecules m⁻² of silica support. The specific surface area of the samples is 260 m² g⁻¹. The XRD spectra of all three samples are similar and show hexagonal CdS on amorphous SiO₂. The broadening of XRD lines indicates very small CdS crystals.

When the CdS/SiO₂ samples were platinized in situ they evolved only a little hydrogen from water–methanol–KOH (0.01 M) solution under visible (λ ≥ 435 nm) irradiation and the reaction stopped after about 40 μL of hydrogen had been evolved. There is no evidence that this hydrogen was produced catalytically. Unfortunately, no products other than hydrogen were detected and therefore we cannot infer a mechanism.

In the absence of KOH and platinum, no hydrogen was found during visible light illumination of CdS/SiO₂.

3.3. Hydrogen Photoevolution from Water–Methanol Solution on Physically Mixed CdS/SiO₂ and Pt/TiO₂/SiO₂. In situ photoplatinization of TiO₂/SiO₂ from H₂PtCl₆ solution was the first step in this set of experiments. It was established earlier (from the time dependence of the rate of hydrogen evolution) that the process is complete after 1 h of irradiation. After platinization, CdS/SiO₂ and KOH were added to the suspension of Pt/TiO₂/SiO₂ in water–methanol, and the slurry was deaerated under sonication and irradiated with visible light (λ ≥ 435 nm).

The rates of hydrogen evolution for these physical mixtures of various Pt/TiO₂/SiO₂ and various CdS/SiO₂ catalysts are shown

TABLE II: Hydrogen Evolution from Water–Methanol on Physically Mixed CdS/SiO₂ and Platinized TiO₂/SiO₂ under Visible Irradiation^a

catalyst	H ₂ yield, μL	
	1 h	2 h
Pt/TiO ₂ /SiO ₂ (400)	44	115
CdS/SiO ₂ (110)		
Pt/TiO ₂ /SiO ₂ (400)	76	151
CdS/SiO ₂ (300)		
Pt/TiO ₂ /SiO ₂ (400)	86	180
CdS/SiO ₂ (400)		
Pt/TiO ₂ /SiO ₂ (110)	30	80
CdS/SiO ₂ (400)		
Pt/TiO ₂ /SiO ₂ (300)	50	120
CdS/SiO ₂ (400)		

^a Reaction conditions: 10 mg of TiO₂/SiO₂; 0.4 wt % Pt (in situ photoplatinization); 10 mL of 1:1 H₂O–MeOH–0.01 M KOH; light source: 450-W Xe lamp, 420-nm cutoff filter.

in Table II. The highest reaction rate was found when CdS/SiO₂ annealed at 400 °C was mixed with in situ photoplatinized TiO₂/SiO₂ (400). Moreover, the reaction rate increased with time during a 2-h irradiation period. Similar increases were observed for all of the mixed systems.

A separate experiment established that hydrogen evolution from physically mixed CdS/SiO₂ and Pt/TiO₂/SiO₂ suspended in aqueous methanol was catalytic. During a long-term experiment (7 days) the rate of H₂ evolution was 31 μL H⁻¹ and did not change with time (the evolved hydrogen was analyzed in 12-h intervals). The turnover number (the ratio of moles of H₂ produced to the moles of CdS which acted as a catalyst) was 9.1 after 7 days or irradiation.

When a mixture of CdS/SiO₂(400)–Pt/TiO₂/SiO₂(400) was irradiated in water–methanol (1:1) in the absence of KOH, only 1/5 of the previously observed amount of hydrogen was found. No hydrogen was evolved when CdS/SiO₂ was mixed with non-platinized TiO₂/SiO₂ and irradiated.

The following evidence shows that the activity cannot be caused by small particles of Pt coming off the original particles and becoming attached to CdS. (1) Platinization of a mixture of CdS and TiO₂ particles gave a material with very poor hydrogen production activity upon visible light irradiation. (2) Separately platinized CdS and TiO₂ particles, when physically mixed and irradiated with wavelengths >435 nm, showed very low hydrogen activity. (3) Adding tiny amounts of chloroplatinic acid (1 to 2% of the usual amount) to the mixture of platinized TiO₂ and CdS reduced the activity for hydrogen production.

3.4. Quantum Efficiency of Hydrogen Photoevolution on Pt/TiO₂/SiO₂–CdS/SiO₂. In a separate experiment, the irradiation was performed with a 200-W high-pressure Hg lamp and a 420-nm cutoff filter. Among the four spectral lines (435.8, 546.1, 577.0, and 690.7 nm) which passed through the filter, only 435.8 nm was efficient for both CdS band gap irradiation and for uranyl oxalate actinometry.²⁷ The longer wavelength lines were beyond the energy barrier for CdS^{28–30} and for UO₂²⁺.^{24,31} By uranyl actinometry, the light flux was 2.01 × 10¹⁶ quanta s⁻¹. The quantum efficiency for H₂ evolution from water–methanol–0.01 M KOH with illuminated Pt/TiO₂/SiO₂(400)–CdS/SiO₂(400) was 1.1%. The value of quantum efficiency was not corrected for light scattering by the catalyst particles.

3.5. Agglomeration of CdS/SiO₂ and Pt/TiO₂/SiO₂ in Hydrogen Evolution. To determine whether agglomeration is critical for efficient hydrogen evolution, the amount of CdS/SiO₂ adsorbed on platinized TiO₂/SiO₂ pellets was determined. Since the total surface area of the pellets (taken from methylene blue adsorption

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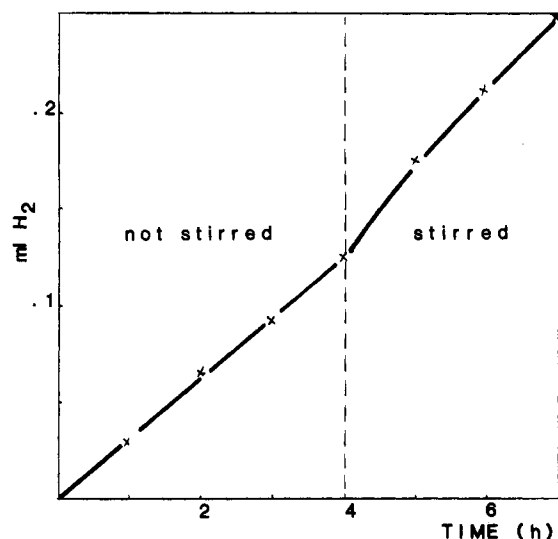


Figure 2. Hydrogen evolution rates on physically mixed CdS/SiO₂(400) and Pt/TiO₂/SiO₂(400). Reaction conditions: 10 mg of Pt/TiO₂/SiO₂(400); 20 mg of CdS/SiO₂(400); 0.4 wt % Pt; 30 mL of 1:1 H₂O:MeOH:0.01 M KOH; light source: 1000-W Xe lamp, 435-nm cutoff filter; 90 mW cm⁻² flux. The temperatures given in parentheses are the catalyst annealing temperatures.

measurements) was close to that of 10 mg of TiO₂/SiO₂ powder (0.086 and 0.11 m², respectively), the same amount of hexachloroplatinic acid was used for photoplatinization of the pellets. A small amount of CdS/SiO₂(400) was found on the pellets: 0.042 mg on the pellets which had been exposed to the light ($\lambda \geq 435$ nm) and 0.035 mg on the pellets which were kept in the dark. The influence of illumination on the extent of CdS/SiO₂ adsorption is not clear, although the differential absorption is real and reproducible. In either case, adsorption of CdS/SiO₂ on Pt/TiO₂/SiO₂ pellets (or the agglomeration in the case of a catalyst suspension) should be considered in the hydrogen photoproduction mechanism.

Nearly the same rate of hydrogen evolution was observed when a slurry of CdS/SiO₂-Pt/TiO₂/SiO₂ in water-methanol-KOH was stirred and when it was not stirred (see Figure 2). During the experiment the upper layer of the catalyst suspension was irradiated from the side wall of the reaction cell. The observed result confirms the importance of the agglomeration of the catalyst particles for the rate of the photoreaction: if no agglomeration occurs the reaction rate should be much higher during stirring because of enhanced interparticle collisions.

3.6. The Role of the Wide-Band-Gap Semiconductor on Hydrogen Photoevolution on CdS/SiO₂ Physically Mixed with Separately Supported Platinum. Three silica-supported oxide semiconductors were prepared: ZnO/SiO₂, SnO₂/SiO₂, and WO₃/SiO₂. A loading of 1.15×10^{-3} mol g⁻¹ of SiO₂, as for TiO₂, was used. The three catalysts, annealed at 400 °C in air, differ only slightly in their specific surface areas: ZnO/SiO₂, 230 m² g⁻¹; SnO₂/SiO₂, 170 m² g⁻¹; and WO₃/SiO₂, 240 m² g⁻¹. For comparison, the specific surface area of TiO₂/SiO₂, annealed at the same temperature, was 260 m² g⁻¹. XRD spectra show that both ZnO and SnO₂ are amorphous, whereas WO₃ is crystalline with lines similar to those reported previously by Drobasheva et al.³³

These three semiconductors were chosen because their conduction bands are more positive than the redox potential of H₃O⁺/H₂ couple^{25,34-41} (see Figure 4). Thus, if their conduction

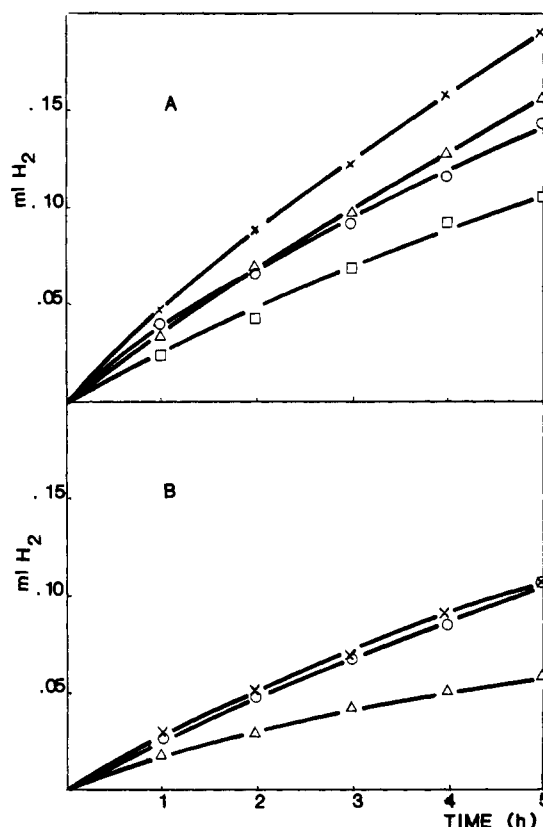


Figure 3. Hydrogen evolution rates vs. time on physically mixed CdS/SiO₂(400 °C) and separately supported platinum: (A) x, Pt on TiO₂/SiO₂(400 °C); o, Pt on SnO₂/SiO₂(400 °C); Δ, Pt on ZnO/SiO₂(400 °C); □, Pt on WO₃/SiO₂(400 °C); (B) o, Pt on SiO₂ impregnation method; x, Pt on TiO₂/SiO₂ impregnation method; Δ, Pt on SiO₂ homogeneous photodecomposition of H₂PtCl₆. Reaction conditions: 10 mg of Pt/support; 20 mg of CdS/SiO₂(400); 0.4 wt % Pt; 30 mL of 1:1 H₂O:MeOH:0.01 M KOH; light source: 1000-W Xe lamp, 435-nm cutoff filter; 90 mW cm⁻² flux.

bands accept electrons from photoexcited CdS, hydrogen evolution should not occur. All three oxides are wide-band-gap semiconductors with E_g similar to (ZnO, WO₃) or higher (SnO₂) than that of titania.

The activity of ZnO/SiO₂, SnO₂/SiO₂, and WO₃/SiO₂ in hydrogen evolution under UV irradiation was measured. In each case, 10 mg of catalyst was mixed with 20 μL of H₂PtCl₆ solution (0.002 g of Pt cm⁻³) and with 30 mL of water-methanol (1:1) solution. The suspension was deaerated in flowing argon under sonication and irradiated with a 200-W high-pressure mercury lamp for 1 h. No hydrogen was found after that time for any of the samples.

Next, potassium hydroxide was added (the resulting solution was 0.01 M KOH) and irradiated. Again, none of the catalysts evolved hydrogen from a water-methanol-KOH mixture. This is very important because the experiments with physically mixed CdS/SiO₂ and platinized ZnO/(SnO₂ or WO₃) were also performed in the presence of potassium hydroxide. The darkening of the powders during the illumination indicated that the photoplatinization had occurred.

Evolution of H₂ on physically mixed CdS/SiO₂ and Pt/ZnO/SiO₂ (or Pt/SnO₂/SiO₂ or Pt/WO₃/SiO₂) was observed in experiments paralleling those described earlier for CdS/SiO₂-Pt/TiO₂/SiO₂. The hydrogen evolution rates on physically mixed CdS/SiO₂ and Pt/TiO₂(ZnO, SnO₂, or WO₃)/SiO₂ are shown in Figure 3A. Although platinized ZnO/SiO₂, SnO₂/SiO₂, and WO₃/SiO₂ do not produce hydrogen when they are irradiated with UV light, their activity for H₂ evolution when physically

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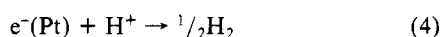
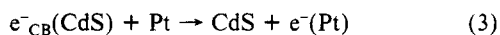
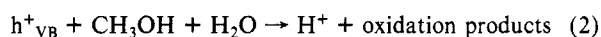
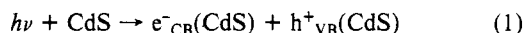
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mixed with visible light irradiated CdS/SiO₂ is relatively high. Moreover, if we take into account the specific surface area of the samples, the following specific rates of hydrogen production of the platinized metal oxide surface are obtained: 14 μL of H₂ m⁻² h⁻¹ for Pt/TiO₂/SiO₂, 14 μL m⁻² h⁻¹ for Pt/ZnO/SiO₂, 16 μL m⁻² h⁻¹ for Pt/SnO₂/SiO₂, and 9 μL m⁻² h⁻¹ for Pt/WO₃/SiO₂.

Figure 3B shows the rates of hydrogen photoproduction on Pt/SiO₂ and Pt/TiO₂/SiO₂ (0.4 wt % Pt, prepared by impregnation of the support with H₂PtCl₆ solution followed by annealing in oxygen at 400 °C for 1 h and reduction in hydrogen at 400 °C for 1 h) in a physical mixture with CdS/SiO₂(400). It is surprising that both Pt/SiO₂ and Pt/TiO₂/SiO₂, prepared in the same manner, show the same activity. The third curve represents similar results using Pt/SiO₂ (0.4 wt % Pt) prepared by homogeneous photodecomposition of hexachloroplatinic acid (λ = 254 nm) in the suspension with SiO₂ in water-methanol (1:1) solution. This shows that the activity depends on the platinization method. Presumably photon absorption by chloroplatinic acid leads to different Pt-particle morphology than photon absorption by TiO₂.

4. Discussion

We now seek to rationalize the above results. The improved activity of the separately supported Pt and CdS can be understood in terms of decreased electron-hole recombination rates. The platinum collects electrons from the conduction band of excited CdS supported on a separate (but weakly agglomerated) particle. The holes in the valence band of CdS react with methanol and water giving alcohol oxidation products (HCHO, CO, and CO₂, according to Kawai et al.^{42,43}). Hydrogen ions are reduced by electrons on platinum particles and gaseous hydrogen is catalytically evolved. These and earlier results^{8-10,35,36} are consistent with the following mechanistic outline:



Our results indicate that reactions involving indirect transfer from CdS to Pt via TiO₂ are not important.

The interparticle electron transfer from the conduction band of CdS to separately supported platinum can be understood if we compare the energy of electrons in CB of CdS (+4 eV below the vacuum level) and of E_F of platinum, which for unsupported Pt powder is approximately 5.6 eV.²⁵ The last value can differ slightly for semiconductor-supported platinum because of the phenomena described by Aspnes and Heller.³⁵ Electron transfer from an excited CdS suspension to a platinum electrode has been observed previously,⁴⁴ although the extent of the electron flux was altered by the applied external potential.

The role of TiO₂ and the other wide-band-gap semiconductors cannot be explained simply. In the case of titania the relative positions of the conduction bands of CdS and TiO₂ (see Figure 4) potentially allows the empty CB of TiO₂ to collect electrons from the CB of excited CdS particles. In fact, electron transfer from the CB of irradiated CdS to TiO₂ has been reported by Gerischer and Luebke.⁴⁵ The next step of the overall reaction

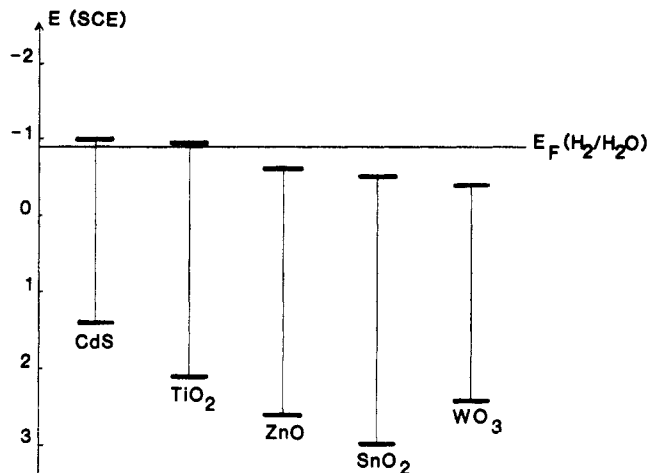


Figure 4. Band edges of CdS, TiO₂, ZnO, SnO₂, and WO₃ at pH 11 shown relative to the potential of the normal hydrogen electrode.³³⁻⁴¹

would be electron passage from CB of TiO₂ to the platinum islands supported on the titania. However, since the activity of platinum supported on ZnO, SnO₂ and WO₃ is relatively high and similar to that on Pt/TiO₂, this possibility cannot be an absolute requirement. If the electrons moved from CB of CdS to that of ZnO, SnO₂, or WO₃ as is thermodynamically plausible (Figure 4), they would be insufficiently energetic to reduce H₃O⁺ ions. Since H₂ is evolved equally well in all the mixed systems, there is no compelling reason to conclude that the conduction band of the added metal oxide is involved.

The high activity of the photodeposited platinum on the wide-band-gap semiconductors (compared to impregnated Pt) is probably caused by its different distribution (morphology) on the support. The wide-band-gap semiconductors are active during photoplatinization, causing a Pt distribution suitable for H₂ evolution. This is consistent with the observation that, when mixed with CdS/SiO₂ and irradiated with visible light, the specific activities of Pt/TiO₂/SiO₂, Pt/ZnO/SiO₂, Pt/SnO₂/SiO₂, and Pt/WO₃/SiO₂ are very similar. Moreover, as discussed above we find that the deposition of platinum on SiO₂ and TiO₂/SiO₂ using impregnation gives materials with equal activities.

Conclusions

The deposition of the oxides of Ti, Zn, Sn, and W onto silica gives high surface area materials with nearly equal specific surface areas. This permits comparison of the catalytic properties of different supported oxides. The deposition of platinum on these metal oxide films on separate SiO₂ particles gives rise to the hydrogen evolution when physically mixed with visible light irradiated CdS/SiO₂. The catalytic properties of supported platinum depend on its distribution on the support. The wide-band-gap oxide semiconductors do not take part in the electron transfer from excited CdS to the platinum islands; rather, the evidence points to *direct transfer* from CdS to Pt. The semiconductor metal oxides play a role in obtaining a platinum distribution suitable for hydrogen evolution. An important factor in hydrogen photoevolution activity for physically mixed CdS/SiO₂ and separate particles of Pt/oxide/SiO₂ systems is the agglomeration of the particles of the two catalysts.

Acknowledgment. This work was supported by the Gas Research Institute.

Registry No. ZnO, 1314-13-2; SnO₂, 18282-10-5; WO₃, 1314-35-8; TiO₂, 13463-67-7; CdS, 1306-23-6; SiO₂, 7631-86-9; H₂, 1333-74-0; H₂PtCl₆, 16941-12-1; methanol, 67-56-1; water, 7732-18-5.

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