

Preparation and Photocatalytic Properties of Silica-Supported Fine CdS Powders

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Summary. Silica-supported cadmium sulfide, highly active in hydrogen photogeneration from water-methanol-KOH solution, was prepared by sulfidation of Cd^{2+} -impregnated SiO_2 . The samples consisted of colloidal-size hexagonal crystallites of CdS on amorphous SiO_2 . A blue shift of a light absorption edge was observed for the samples with lower CdS content.

Keywords. Cadmium sulfide; preparation; photocatalytic activity.

Herstellung und photokatalytische Aktivität von feinen CdS-Pulvern auf SiO_2

Zusammenfassung. Es wurde Cadmiumsulfid auf Kieselgel durch Sulfidierung von Cd^{2+} -imprägniertem SiO_2 hergestellt, das eine außerordentliche Aktivität bei der Wasserstoff-Photogenerierung aus Wasser-Methanol-KOH-Lösungen zeigte. Der Katalysator bestand aus hexagonalen CdS-Kristalliten von kolloidalen Ausmaßen auf amorphem SiO_2 . An Proben mit geringerem CdS-Gehalt wurde eine Blauverschiebung der Lichtabsorption an der Absorptionskante beobachtet.

Introduction

Photoactive semiconductors with colloidal dispersity have drawn attention of scientists because of their enormously high activity on the one hand [1–5] and on size quantization effect on the other [2, 6–9]. The first effect is on account of high carrier mobility, efficient separation of photogenerated electrons and holes and a very large specific surface area which favours semiconductor-electrolyte interaction. Concerning the second effect, a blue shift of photoabsorption and photoluminescence spectra is shown by small colloidal particles such as CdS, ZnS or TiO_2 (below 100 Å). The effect is connected to the special electronic properties due to quantized motion of the charge carriers in a restricted area.

Several methods to prepare solutions of colloidal semiconductor particles showing sufficiently good stability have been proposed [2, 7, 8, 10]. Preparation of solid semiconductors with colloidal dispersion has been also reported [3, 5, 11–13]. For that purpose the authors used a number of supports like cellulose, polyurethane, Nafion, porous Vycor glass, clay or molecular sieves.

In previous studies fine CdS or TiO_2 powders were prepared by precipitation of the compounds from a solution in the presence of colloidal SiO_2 , subsequent

filtration, drying and calcination at appropriate temperature [14–16]. In this paper a new method of preparation of small CdS particles on SiO₂ support is presented along with some physico-chemical properties and photoactivity of the resulting samples.

Experimental Part

Sample Preparation

CdSiO₂. Appropriate amounts of Cd(NO₃)₂ · 4 H₂O were dissolved in 250 ml H₂O and 25% ammonia water was added until the white precipitate was dissolved (*pH* 8). 10 g SiO₂ (Aerosil 200, Degussa) was added to the solution. The slurry was mixed and heated in a water bath to dryness. For the second series of samples Cd(CH₃COO)₂ · 2 H₂O was used instead of cadmium nitrate. No ammonia water was added in this case. Similarly like above the solutions were mixed with 10 g SiO₂ and heated to dryness. All samples were then heated in a stream of H₂S (Fluka): firstly at 473 K for 1 h to remove the residue of NH₄NO₃ or CH₃COOH, and then at 673 K for 2 h. The samples were cooled down in a stream of H₂S and flushed with argon.

Pt/SiO₂. The silica supported platinum catalyst containing 2 wt.% Pt, was prepared by impregnation of SiO₂ (Aerosil 200, Degussa) with an appropriate amount of H₂PtCl₆ solution followed by reduction in hydrogen at 473 K for 2 h.

CdS/SiO₂ Characterization

XRD measurements were performed on a TUR MG2 powder diffractometer using CuK_α radiation. BET specific surface areas were measured by nitrogen adsorption at 77 K using a dynamic method. UV and visible reflection spectra were taken on a Specord M-40 spectrometer in a wavelength range 200–800 nm. MgO powder was used as a standard.

Studies of Hydrogen Photoproduction

The reaction was carried out in the way described previously [18–21] in a 100 ml volume bottle shape Pyrex reaction cell equipped with an entrance-exit system for flowing argon. Before measurements 0.04 g CdS/SiO₂ and 0.02 g Pt/SiO₂ were added to the reaction cell which contained 65 ml H₂O, 25 ml CH₃OH and 10 ml 1.0 *m* KOH. The suspension was deaerated under flowing argon and sonicated. The reaction cell was placed in a Pyrex water bath at a constant temperature 298 ± 1 K and irradiated with a 180 W medium pressure mercury lamp. The CdS/SiO₂ and Pt/SiO₂ particles were suspended using a magnetic stirrer. Argon, which flowed through the cell during the reaction was purified on columns containing activated copper to remove traces of oxygen. Evolving hydrogen was analyzed with a gas chromatograph using a 2 *m* column filled with an activated charcoal, operated at 313 K and with argon as a carrier gas.

Incident light flux was measured by an oxalateuranyl actinometer [18–21]. The light flux was found to be 15.6 · 10⁻² μmol quants per second.

All chemicals used were p. a. grade. The water used in the hydrogen photoproduction experiments was doubly distilled from a quartz vessel.

Results and Discussion

Six CdS/SiO₂ samples were prepared using different salts of cadmium: Cd(NO₃)₂ and Cd(CH₃COO)₂. Characteristics of the samples and the sample code are given in Table 1.

Table 1. Some characteristics of CdS/SiO₂ samples

Sample code	CdS content ^a		Cryst. size ^b Å	Sp. surf. area m ² g ⁻¹	Amount of H ₂ ^c cm ³ h ⁻¹ STP
	mol CdS /1 g SiO ₂	wt. %			
14 CdSA	1.15 · 10 ⁻³	14.5	400	156	1.2
1.7 CdSA	1.15 · 10 ⁻⁴	1.7	—	167	0.29
0.17 CdSA	1.15 · 10 ⁻⁵	0.17	—	169	0.03
14 CdSN	1.15 · 10 ⁻³	14.5	200	134	2.4
1.7 CdSN	1.15 · 10 ⁻⁴	1.7	—	153	0.45
0.17 CdSN	1.15 · 10 ⁻⁵	0.17	—	156	0.05

^a The values estimated from the amounts of Cd²⁺ salts and SiO₂ taken for sample preparation

^b Calculated from a Scherrer formula

^c At a steady of the reaction

The preparation method consisted of two steps: (i) impregnation of colloidal SiO₂ (Aerosil 200, Degussa) with a solution of Cd²⁺ followed by evaporation of water and drying in a water bath; (ii) sulfidation of Cd²⁺-impregnated SiO₂ in a stream of H₂S.

In the first step a very thin film of cadmium(II) compound was formed on the surface of the colloidal SiO₂. In the second, formation of small CdS islets weakly attached to the support was expected.

It is well known that the surface of silica, unlike alumina, does not form strong bonds with supported compounds. Therefore, rather mixed CdS and SiO₂ particles than silica-supported cadmium sulfide were a result of the precipitation method used before [14–16]. However, also in the case of the preparation method used here, some separation of CdS and SiO₂ from the weakly bonded CdS/SiO₂ particles can take place, especially when the samples are stirred and illuminated in a water-methanol-KOH solution; see below.

The role of a large surface area colloidal SiO₂ (170 m² g⁻¹ as measured by the BET method) was to assure the conditions for formation of very small CdS particles. If we take into account that the monolayer coverage of the support by CdS is in the order of 10¹⁸ particles per 1 m², the uniform CdS film on the surface of SiO₂ can be formed only for the highest CdS content (1.15 · 10⁻³ mol CdS per 1 g CdS, which gives a value of 4 · 10¹⁸ Cd-atoms per 1 m²). The coverage of the SiO₂ surface by CdS for samples with lower cadmium sulfide contents (1.15 · 10⁻⁴ and 1.15 · 10⁻⁵ mol CdS per 1 g SiO₂) is much lower than a monolayer (about 0.5–0.01, respectively). Hence isolated islets of CdS are expected to exist on the surface of SiO₂.

The formation of very small CdS crystallites in CdS/SiO₂ was confirmed both by XRD measurements and by UV-visible reflectance spectroscopy. Well defined XRD reflexes of a hexagonal CdS structure are seen only in the spectra of 14 CdS (A and N series; the spectra are not shown in the paper). The reflexes are broad; particle sizes calculated from the Scherrer formula are: 400 Å for 14 CdSA and 200 Å for 14 CdSN. (100) and (101) lines are quenched partly in the spectrum of 14 CdSN which is indicative of not well developed CdS hexagonal structure.

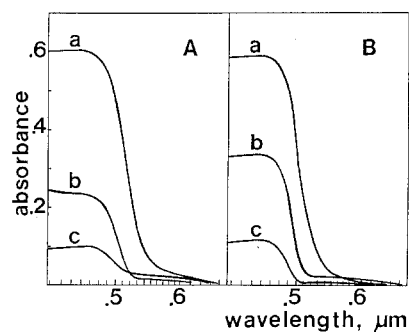


Fig. 1. UV-visible reflection spectra of CdS/SiO₂ taken on a Specord M-40. **A** Samples prepared from cadmium acetate, **B** samples prepared from cadmium nitrate. *a* 14 CdS, *b* 1.7 CdS, *c* 0.17 CdS

The XRD lines are very small for 1.7 CdS-samples; the positions of the lines also indicate the CdS hexagonal structure. No XRD lines were found in the spectra of 0.17 CdS (A and N). However, the existence of hexagonal CdS in these samples is also expected (note that the samples show light absorption edges characteristic for a crystal CdS; see below). The XRD spectra of the all six samples show a very broad line with a maximum at 2Θ about 13° indicative of the presence of amorphous SiO₂.

The colour of the samples changes from yellow-orange for 14 CdS's to pale-yellow-green for 0.17 CdS's. The changes are on account of a blue shift of light absorption edges, see Fig. 1. It was mentioned above that the blue shift of the light absorption is shown by crystallites with a particle size below 100 Å. Therefore, the CdS crystallites in the 1.7 CdS and 0.17 CdS samples are less than 100 Å. 14 CdS samples do not show a blue shift in their light absorption edges — according to Ref. [6] the “bulk” CdS crystallites show an absorption edge at about 510 nm which is related to their forbidden gap energy of 2.4 eV.

If we sum up the above considerations it can be concluded that the CdS/SiO₂ samples consist of very small CdS crystallites supported on amorphous SiO₂. The size of the crystallites decreases with a decrease of CdS content in the samples. A blue shift of the light absorption edges is more pronounced for the samples prepared from cadmium nitrate; see Fig. 1.

Photoactivity of the samples was studied in the reaction of hydrogen generation from water-methanol-0.1 *m* KOH in the presence of Pt/SiO₂ as a H₂-evolution catalyst. Amounts of CdS/SiO₂ and Pt/SiO₂, the *pH* of the solution and a

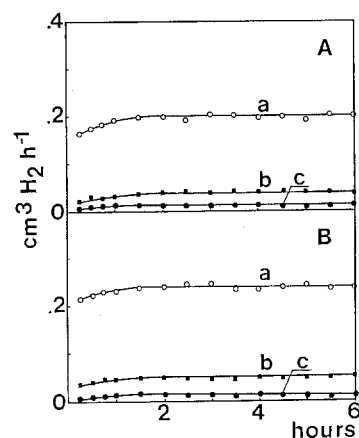


Fig. 2. Rates of H₂ photoproduction vs. time. **A** samples prepared from cadmium acetate, **B** Samples prepared from cadmium nitrate. *a* 14 CdSN, *b* 1.7 CdSN, *c* 0.17 CdSN. Reaction conditions: H₂O : MeOH = 3 : 1; 0.1 *m* KOH; 0.04 g CdS/SiO₂; 0.02 g Pt/SiO₂ (2 wt.% Pt); 100 ml volume; 298 K; 180 W medium pressure Hg lamp; GC analysis of H₂

water : methanol ratio of 3 : 1 were chosen experimentally to ensure high reaction yield. The details of the optimization procedure have been published elsewhere [14, 15, 18 – 21].

The results of the study of hydrogen photoproduction are shown in Table 1 and in Figs. 2A and 2B. The highest activity in the process was shown by 14CdSN: 0.04 g of the sample mixed with 0.02 g Pt/SiO₂ produced as much as 2.4 cm³ H₂ per 1 h. A quantum yield of the reaction defined as the ratio of the hydrogen produced to the incident light flux was 0.38. It was observed before [14] that 10 mg CdS/SiO₂, prepared by precipitation of the sulfide, produced about 0.2 cm³ H₂ h⁻¹ under similar conditions when mixed with 0.05 g Pt/SiO₂. Therefore the activity of the mass unit of the 14CdSN sample is three times higher.

It was checked in separate experiments that the activity of the above sample did not undergo any changes during 30 hours of illumination in the water-methanol-0.1 M KOH medium. If one takes into account the amount of hydrogen produced during the 30 hours and the amount of CdS in 0.04 g CdS/SiO₂ one can calculate that 1 μmol CdS produced about 83 μmol of hydrogen. This showed that the process was catalytic.

The samples prepared from the nitrate precursor were more active than these prepared from cadmium acetate. In both series of the samples the activity lowered along with lowering of the contents of CdS. On the contrary the specific activity (the activity of the mass unit of CdS) is higher for the samples containing less CdS. This is probably caused by the above mentioned enhancement of the semiconductor-electrolyte interaction. A blue shift of the light absorption edges characteristic for these samples should not influence their photoactivities (the same lines from the spectra of the mercury lamp are absorbed by all samples).

Concluding, the sulfidation of Cd²⁺-impregnated colloidal silica gives highly photoactive CdS powders which are stable under H₂-photogeneration conditions. The samples consist of colloidal-size cadmium sulfide crystallites supported onto fine SiO₂ powder. The CdS/SiO₂ sample containing 14.5 wt.% CdS with an average crystallite size of 200 Å, which was prepared by sulfidation of Cd(NO₃)₂-impregnated SiO₂, was found to be the most active one in hydrogen photogeneration from water-methanol-KOH solution when mixed with an active H₂-evolution catalyst (Pt/SiO₂). The activity of the sample was very high – the quantum yield of the hydrogen production was as high as 0.38. In the author's opinion the preparation method described in the paper can be recommended for preparing of active cadmium sulfide powders.

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