spite of the presence of OH groups, both surfaces are nonhydrophilic and lipophilic: Water molecules are not attracted to the surface, as they are equally happy in bulk water. On the other hand, the presence of the surface perturbs the water structure sufficiently to create free volume, in which an argon atom (and, hence, a small lipophilic moiety of an organic adsorbent) can dissolve more easily than in the denser bulk water. The wider spacing of cellulose chains allows the 110 surface to expose more of the hydrophobic grooves where lipophilic adsorption takes place. In contrast, the protruding OH groups are less affected by chain packing, so the behavior towards water is similar for both surfaces.

Received: June 8, 2001 [Z 17256]

---

[1] S. Imam, R. V. Green, B. R. Zaidi, *Biopolymers—Utilizing Nature's Advanced Materials*, American Chemical Society, Washington, DC, **1998**.

[2] J. C. Roberts, *The Chemistry of Paper*, Royal Society of Chemistry, Cambridge, **1996**.

[3] T. Heinze, U. Erler, I. Nehls, D. Klemm, *Angew. Makromol. Chem.* **1994**, *215*, 93–106; A. Baar, W. M. Kulicke, K. Szablikowski, R. Kiesewetter, *Macromol. Chem. Phys.* **1994**, *195*, 1483–1492.

[4] F. Müller-Plathe, H. Schmitz, R. Faller, *Prog. Theor. Phys. Suppl.* **2000**, *138*, 311–319.

[5] A. A. Baker, W. Helbert, J. Sugiyama, M. J. Miles, *J. Struct. Biol.* **1997**, *119*, 129–138.

[6] A. A. Baker, W. Helbert, J. Sugiyama, M. J. Miles, *Appl. Phys. A* **1998**, *66*, S559–S563.

[7] A. A. Baker, W. Helbert, J. Sugiyama, M. J. Miles, *Biophys. J.* **2000**, *79*, 1139–1145.

[8] A. Aabloo, A. D. French, *Macromol. Theory Simul.* **1994**, *3*, 185–191.

[9] S. Reiling, J. Brickmann, *Macromol. Theory Simul.* **1995**, *4*, 725–741.

[10] S. K. Cousins, R. M. Brown, Jr., *Polymer* **1995**, *36*, 3885–3888.

[11] A. P. Heiner, J. Sugiyama, O. Teleman, *Carbohydr. Res.* **1995**, *273*, 207–232.

[12] B. J. Hardy, A. Sarko, *Polymer* **1996**, *37*, 1833–1839.

[13] A. P. Heiner, O. Teleman, *Langmuir* **1997**, *13*, 511–518.

[14] A. P. Heiner, L. Kuutti, O. Teleman, *Carbohydr. Res.* **1998**, *306*, 205–220.

[15] J. Ganster, H.-P. Fink in *Polymer Handbook* (Eds.: J. Brandrup, E. H. Immergut, E. A. Grulke), Wiley, New York, NY, **1999**.

[16] J. Sugiyama, R. Vuong, H. Chanzy, *Macromolecules* **1991**, *24*, 4168–4175.

[17] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, J. R. Haak, *J. Chem. Phys.* **1984**, *81*, 3684–3690.

[18] W. F. van Gunsteren, S. R. Billeter, A. A. Eising, P. H. Hünenberger, P. Krüger, A. E. Mark, W. R. P. Scott, I. G. Tironi, *Biomolecular Simulation: The GROMOS96 Manual and User Guide*, vdf, Zurich, **1996**.

[19] F. Müller-Plathe, *Comput. Phys. Commun.* **1993**, *78*, 77–94.

[20] J. R. Grigera, S. G. Kalko, J. Fischbarg, *Langmuir* **1996**, *12*, 154–158.

[21] B. Guillot, Y. Guissani, *J. Chem. Phys.* **1993**, *99*, 8075–8094.

[22] F. Müller-Plathe, *J. Chem. Phys.* **1995**, *103*, 4346–4351.

[23] *Handbook of Chemistry and Physics*, 74th ed. (Ed.: D. R. Lide), CRC Press, Boca Raton, FL, **1993**.

[24] F. Müller-Plathe, W. F. van Gunsteren, *Polymer* **1997**, *38*, 2259–2268.

Electronic Semiconductor–Support Interaction—A Novel Effect in Semiconductor Photocatalysis[**]

Harald Weiß, Asuncion Fernandez, and Horst Kisch[*]

Dedicated to Professor Yasuo Wakatsuki
on the occasion of his 60th birthday

The growing field of semiconductor photocatalysis has moved from basic research to practical applications. Typical examples are the detoxification of air and water[1] and novel organic syntheses[2] photocatalyzed by titania and cadmium sulfide. The photonic efficiency of these transformations largely depends on the ratio of the rate of interfacial electron transfer (IFET) to the rate of recombination of the photogenerated electron-hole pair. It is generally assumed that only substrates adsorbed at the semiconductor surface can participate in the IFET. Therefore in many cases the reaction rate increases when substrate adsorption is improved. A better adsorption was also invoked to rationalize the higher detoxification rates induced by supporting semiconductors like titania onto silica or alumina.[3]

During our work on addition reactions photocatalyzed by semiconductors (semiconductor photocatalysis type B) we observed that precipitation of cadmium sulfide onto silica afforded a much better photocatalyst than the unsupported material. Herein we report on experimental evidence that this enhanced photocatalytic activity does not stem from improved adsorption but rather from an electronic semiconductor–support interaction (SEMSI), which alters the bandgap energy and flatband potential. Whereas electronic catalyst–support interactions are well documented in thermal heterogeneous catalysis, they have been unknown in the field of semiconductor photocatalysis.

Thus, whereas the reaction between cyclopentene (RH) and the Schiff base **1** (Scheme 1)[2d,e] is quite slow in the presence of CdS it becomes about 10 times faster when silica covered with 50% CdS (CdS-50/SiO_2) is used as the photocatalyst. According to the proposed mechanism, the intermediate aminobenzyl and allyl radicals are formed through proton-coupled IFET reactions of the substrates with reactive electrons and holes (e_r^-, h_r^+). Their C–C hetero- and homocoupling lead to **2** and **3** as the major and by-product, respectively.[2d,e]

---

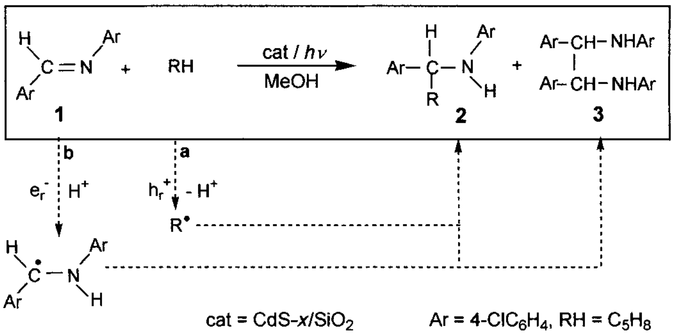
[*] Prof. Dr. H. Kisch, Dipl.-Chem. H. Weiß
Institut für Anorganische Chemie der Universität Erlangen-Nürnberg
Egerlandstrasse 1, 91058 Erlangen (Germany)
Fax: (+49) 9131-8527363
E-mail: kisch@chemie.uni-erlangen.de

Dr. A. Fernandez
Instituto de Ciencia de Materiales de Sevilla
Dpto. Química Inorgánica
Centro de Investigaciones Científicas Isla de la Cartuja
Avda. Américo Vespucio s/n, 41092 Sevilla (Spain)

[**] This work was supported by the Volkswagen-Stiftung, the Deutsche Forschungsgemeinschaft, and Fonds der Chemischen Industrie. Helpful discussions with D. Meissner are gratefully acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

1433-7851/01/4020-3825 $ 17.50+.50/0



Scheme 1. Photoaddition of cyclopentene (RH) to the Schiff base **1**.

Silica-supported photocatalysts CdS-*x*/SiO$_2$ containing 50, 30, and 12 wt% of CdS were prepared by impregnating SiO$_2$ with cadmium sulfate and successive precipitation with sodium sulfide. Specific surface areas of the resulting materials were in the range of 157–270 m^{2}g^{-1}. To obtain the bandgap energy, diffuse reflectance spectra were measured and the modified Kubelka–Munk function $[F(R_\infty)h\nu]^2$ was plotted against $h\nu$.[4] Surprisingly, the bandgap of CdS employed (2.25 eV) increases to 2.34, 2.38, and 2.43 eV when the coverage varies from 50 to 30 and 12%, respectively (Figure 1, Table 1).[5] The effect does not arise from a quantum size effect, as indicated by the following.

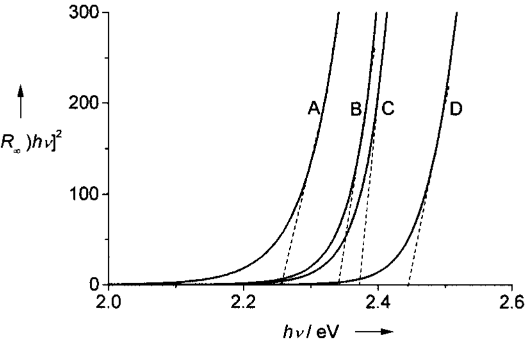


Figure 1. Transformed diffuse reflectance spectra of CdS (A), CdS-50/SiO$_2$ (B), CdS-30/SiO$_2$ (C), and CdS-12/SiO$_2$ (D).

Table 1. Photoelectrochemical data[a] and bandgap energies.

	pH$_0$	U_{fb} [V, NHE][b]	E_{bg} [eV][c]
CdS	9.0	−0.38	2.25
CdS-50	9.0	−0.38	2.34
CdS-30	8.5	−0.41	2.38
CdS-12	3.0	−0.59	2.43

[a] Measured according to ref. [9]. [b,c] Reproducibility was better than ±0.01 V and ±0.02 eV, respectively.

All samples contain micrometer-sized aggregates composed of cubic and amorphous CdS nanoparticles of 6–10 nm.[6] In general, transmission electron micrography in various regions of the powders reveals that with decreasing coverage the aggregates become smaller and more homogeneously dispersed on the silica surface. Representative high-resolution transmission electron micrographs of CdS and CdS-12/SiO$_2$ are displayed in Figure 2. They clearly reveal the presence of CdS nanocrystals having the same average diameter of 6–10 nm both for the unsupported and the lowest coverage photocatalyst. This independence of particle size on coverage is also seen in the X-ray powder diffractograms. For all four samples the peak width is the same.

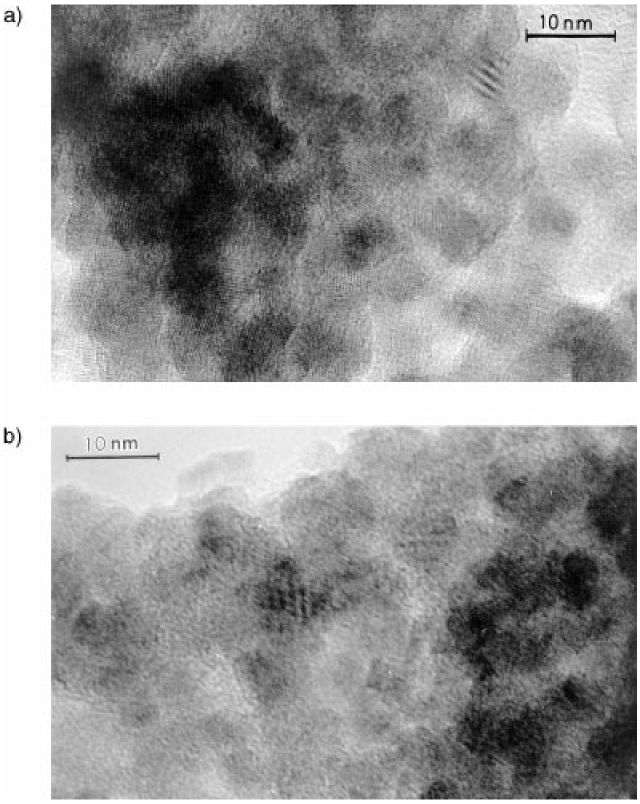


Figure 2. High-resolution transmission electron micrographs of CdS (a) and CdS-12/SiO$_2$ (b).

The bandgap energy does not change when silica and CdS are ground in a mortar or when silica is first silylated with Me$_3$SiCl before impregnation with cadmium ions. In both cases the photocatalytic activity corresponds to that of unmodified CdS. From this it is evident that the observed bandgap shifts originate from an electronic interaction between CdS and SiO$_2$, which is induced by formation of [Si]-O-Cd bonds through reaction of surface OH groups with cadmium ions. The presence of these bonds is indicated by the disappearance of the broad IR absorption band of silica at 1190 cm^{-1}, when the the silica is loaded with CdS.[7] Accordingly, it is expected that upon addition of sulfide, growth of the CdS particles starts at these surface-bound cadmium ions. Of the resulting aggregate only the non surface-bound part is sensitive to the diffuse reflectance measurement and it is assumed that the electronic influence of the surface-bound CdS layer on this part should be stronger for the smaller aggregate. As expected, the strongest blue-shift is measured for CdS-12/SiO$_2$.

To test whether the larger bandgap is caused by a shift of the valence or conduction band edges, the position of the flatband potential (U_{fb}) of the photocatalysts was determined by the methods of Bard[8] and Roy[9] through measuring photocurrent and photovoltage as a function of the pH value. The values obtained by the latter method are summarized in Figure 3 and Table 1. From the corresponding inflection points (pH$_0$) the U_{fb} values are easily obtained and converted to the value at pH 7.[10] A lower pH$_0$ value corresponds to a more negative flatband potential.

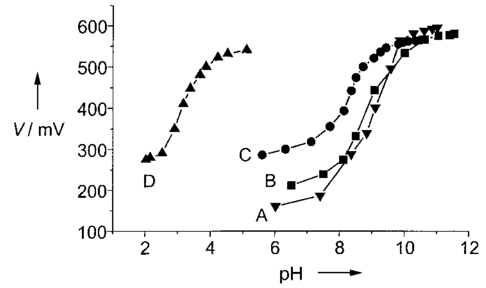


Figure 3. Dependence of photovoltage (vs. NHE) on the pH value of the electrolyte. CdS (A), CdS-50/SiO$_2$ (B), CdS-30/SiO$_2$ (C), and CdS-12/SiO$_2$ (D).

Whereas the flatband potential of -0.38 V measured for CdS-50/SiO$_2$ does not differ from that of unsupported CdS, it is shifted to -0.41 and -0.59 V in the case of CdS-30/SiO$_2$ and CdS-12/SiO$_2$, respectively. In the same sequence the relative initial rate[11] increases from 1.0 through 10 and 11 to 12 (Figure 4). Since the tenfold rate increase found for CdS-50/SiO$_2$ cannot be caused by a change of the position of the flatband potential, which is the same as for unmodified CdS, it may originate from an anodic shift of the valence band edge, which would result in an acceleration of the oxidative IFET reaction (path a, Scheme 1).

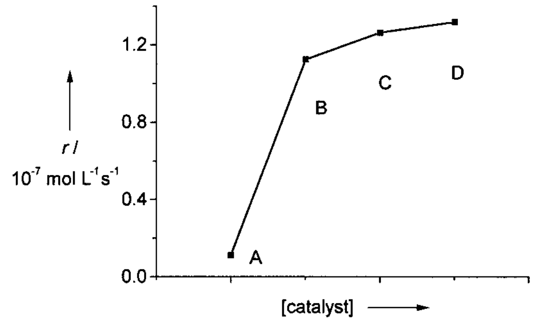


Figure 4. Dependence of reaction rate for formation of **2** on the coverage. CdS (A), CdS-50/SiO$_2$ (B), CdS-30/SiO$_2$ (C), and CdS-12/SiO$_2$ (D).

Another possibility is that the silica support may increase the rate through inducing a better substrate adsorption. To test this hypothesis the adsorption of **1** and cyclopentene onto CdS and CdS-50/SiO$_2$, suspended in methanol, was measured. Since no significant differences were found, it is unlikely that the observed rate increase arises from an improved adsorption. More likely, it is a consequence of an anodic shift of the valence band edge, which should render the reactive hole a better oxidizing agent and therefore accelerate the oxidative IFET reaction. Since the valence band has predominantly sulfur character, this shift should increase the binding energy of the sulfur 2p electrons. In fact, values of 162.7, 162.9, and 163.2 eV were measured for CdS, CdS-50/SiO$_2$, and CdS-30/SiO$_2$, respectively. As in the case of the bandgap shift, the SEMSI effect is stronger for the sample with a better dispersion of CdS onto the support surface.

Based on these experimental data, it is concluded that the enhanced photocatalytic activity of silica-supported CdS is attributed to an electronic semiconductor–support interaction mediated through surface [Si]-O-Cd-S bonds.

Experimental Section

Cadmium sulfide was prepared as described in reference [2e]. Neutral SiO$_2$ of specific surface area of 360 m^{2}g^{-1} was obtained commercially. Supported samples were prepared by stirring SiO$_2$ with an aqueous CdSO$_4$ solution of appropriate concentration overnight, followed by addition of dissolved sodium sulfide.[2e] Transmission electron microscopy measurements were carried out with a PHILIPS CM200 microscope working at 200 kV. The samples were dispersed in ethanol by ultrasound and cast on a copper grid coated with a carbon film. XPS spectra were recorded by using a VG-Escalab 210 Spectrometer ($\Delta E = cte$ mode, pass energy of 50 eV, $\mathrm{Mg}_{\mathrm{K}\alpha}$ radiation). The binding energy (BE) reference was taken as the C1s peak from carbon contamination of the samples at 284.6 eV. Rates of this pseudo zero-order reaction were obtained by irradiating a suspension of 4.2 gL^{-1} of CdS or 8.4–35 gL^{-1} of CdS-x/SiO$_2$ in methanol, containing the same total amount of CdS, in the presence of 0.01M of the imine **1** and 0.47M of cyclopentene; product formation was measured by HPLC.[2d]

Received: February 16, 2001
Revised: August 1, 2001 [Z16623]

---

[1] a) *Photocatalytic Purification and Treatment of Water and Air* (Eds.: D. F. Ollis, H. Al-Ekabi), Elsevier, Amsterdam, **1993**; b) M. A. Fox, M. T. Dulay, *Chem. Rev.* **1993**, *93*, 341; c) O. Legrini, E. Oliveros, A. M. Braun, *Chem. Rev.* **1993**, *93*, 671; d) A. Fujishima, K. Hashimoto, T. Watanabe, *TiO$_2$ Photocatalysis. Fundamentals and Applications*, 1st ed., BKC, Tokyo, **1999**.

[2] a) R. Künneth, C. Feldmer, H. Kisch, *Angew. Chem.* **1992**, *104*, 1102; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1039; b) R. Künneth, G. Twardzik, G. Emig, H. Kisch, *J. Photochem. Photobiol. A* **1993**, *76*, 209; c) R. Künneth, C. Feldmer, F. Knoch, H. Kisch, *Chem. Eur. J.* **1995**, *1*, 441; d) W. Schindler, F. Knoch, H. Kisch, *Chem. Ber.* **1996**, *129*, 925; e) W. Schindler, H. Kisch, *J. Photochem. Photobiol. A* **1997**, *103*, 257; f) H. Keck, W. Schindler, F. Knoch, H. Kisch, *Chem. Eur. J.* **1997**, *3*, 1638; g) A. Reinheimer, R. van Eldik, H. Kisch, *J. Phys. Chem. B* **2000**, *104*, 1014; h) "Semiconductor Photocatalysis for Organic Syntheses": H. Kisch, *Adv. Photochem.* **2001**, *26*, 93.

[3] C. Anderson, A. J. Bard, *J. Phys. Chem.* **1997**, *101*, 2611.

[4] B. Karvaly, I. Hevesy, *Z. Naturforsch. A* **1971**, *26*, 245.

[5] This corresponds to onset absorptions of 551, 530, 521, and 510 nm.

[6] A. Reinheimer, A. Fernández, H. Kisch, *Z. Phys. Chem.* **1999**, *213*, 129.

[7] Similar Ti-O-Si cross-linking bonds have been detected at the TiO$_2$–SiO$_2$ interface. G. Lassaletta, A. Fernández, J. P. Espinós, A. R. González-Elipe, *J. Phys. Chem* **1995**, *99*, 1484.

[8] J. R. White, A. J. Bard, *J. Phys. Chem.* **1985**, *89*, 1947.

[9] A. M. Roy, G. C. De, N. Sasmal, S. S. Bhattacharyya, *Int. J. Hydrogen Energy* **1995**, *20*, 627. The powders were suspended in 0.1M KNO$_3$ (50 mL) containing methylviologen dichloride (5 mg).

[10] U_{fb} values for pH 7 were calculated according to ref. [8].

[11] The initial rate induced by CdS was set to 1.0.