

Photochemistry of Colloidal Semiconductors

10. Exclusion Chromatography and Stop Flow Experiments on the Formation of Extremely Small CdS Particles

Ch.-H. Fischer, H. Weller, A. Fojtik*), C. Lume-Pereira, E. Janata, and A. Henglein**)

Hahn-Meitner-Institut für Kernforschung Berlin, Bereich Strahlenchemie, D-1000 Berlin 39, Federal Republic of Germany

Chemical Kinetics / Colloides / Photochemistry / Semiconductors

A solution of Q-CdS (particles of extremely small size, prepared by precipitation in the presence of hexametaphosphate, separated as solid, and redissolved) was fractionated by exclusion chromatography. The various fractions had absorption spectra, in which the maximum of the exciton transition is shifted to shorter wavelengths with increasing elution time. This result proves that the various absorption maxima in the spectrum of Q-CdS are caused by particles of different size. — The development of the absorption spectrum of CdS at different times after the mixing of NaSH and Cd(ClO₄)₂ solutions in the presence of hexametaphosphate was observed with a stop flow apparatus. As the particles grow, the beginning of absorption is shifted to longer wavelengths. Spectra with several absorption maxima are observed in a certain range of hexametaphosphate concentration. The rate and structure of size distribution are dependent on whether precipitation occurs in bulk solution or on the Cd²⁺ loaded metaphosphate matrix.

Introduction

The transition from bulk semiconductor properties to molecular properties with decreasing size of colloidal semiconductor particles has drawn the attention of several laboratories during the last two years [1–14]. Most of the observations of size quantization effects have been made on cadmium sulfide and other metal sulfides such as PbS and HgS. More recently, strong effects were reported for the phosphides and arsenides of cadmium and zinc [8, 10]. The first examples for such size effects in oxides have recently been found for ZnO [11] and MnO₂ [12]. We use to designate materials which show size quantization effects as "Q-materials". In some cases, these materials were also obtained in the solid state [6, 8, 10].

In the presence of metaphosphate anions, very small CdS particles are produced in the reaction of H₂S with Cd²⁺ ions. These small particles are colorless, their optical absorption starting to rise below 400 nm. The absorption spectrum of such a sol often contains several maxima separated by 10 to 20 nm. These maxima have been attributed to exciton absorption in particles of different sizes, and it has been postulated that preferential or "magic" agglomeration numbers exist in the size distribution of such colloids [6].

In the present work, solutions of very small CdS particles are investigated by gel chromatography in order to show that the various absorption maxima are caused by particles

of different sizes. Further, stop flow experiments are carried out to observe the formation of extremely small CdS particles (absorbing in the UV), their growth into larger particles (absorbing in the near UV and the beginning of the visible) and the evolution of their absorption maxima at different times.

Experimental

The experiments on the exclusion chromatography of CdS sols were carried out with a column of 1.0 cm diameter. The stationary phase consisted of three fillings in series of sephacryl gels from Pharmacia, each filling being 30 cm long. The lowest filling consisted of gel S500, followed by S300 and S200 gels, the particle size of all these three materials lying between 40 and 105 μm. The eluent was a 1.2 · 10⁻⁴ M sodium hexametaphosphate solution, the rate of elution was 0.17 ml · min⁻¹. 0.25 ml of the CdS sol were injected. The outcoming solution was continuously monitored with a UV spectrophotometer at 240 nm. Every 7.5 minutes, a new fraction was collected and its absorption measured in a Shimadzu UV 240 spectrophotometer.

A commercial stop flow apparatus, model D-110 Durrum Di-onex, was used in the studies on the reaction of Cd²⁺ with SH⁻ and the following apparatus improvements were made to it. Optical absorption vs. time curves were recorded and stored by a programmable digitizer (7D20, Tektronix). The digitizer was connected to a computer (micro-11, DEC) via an IEEE-488 bus for data analysis and storage. In order to overcome the time consuming procedure of adjusting the photomultiplier light level and the baseline each time the wavelength was changed, the buffer amplifier of the apparatus was replaced by back-off circuitry for automatic baseline compensation and measurement of the background current [15]. In the beginning of the recording, the solution of the preceding experiment was still in the cell. It was removed by the new mixture within a few milliseconds. During this removal the absorption of

*) Home address: Czechoslovak Academy of Science, Prague, Institute of Physical Chemistry and Electrochemistry.

**) To whom corresponding should be directed.

the solution changed, and the photomultiplier current varied correspondingly. The photomultiplier current was compensated to zero during all this time and then the compensation current was kept constant during the following recording. The compensating current was read by the computer and used for the calculation of absorbances.

The sodium hexametaphosphate was a commercial sample (Riedel de Haen). Molarities were calculated using the formula $\text{Na}_6(\text{PO}_3)_6$. However, the sample consisted mainly of much larger polyphosphates up to a chain length of 450 (as cited by the producer).

Results

Exclusion Chromatography

This kind of chromatography is based on the principle that the pores of the stationary phase are less accessible to larger particles. These particles therefore appear in the first fractions. Exclusion chromatography is used for separating synthetic polymers and biopolymers of different sizes. It seems that this method has not yet been applied in inorganic colloid chemistry.

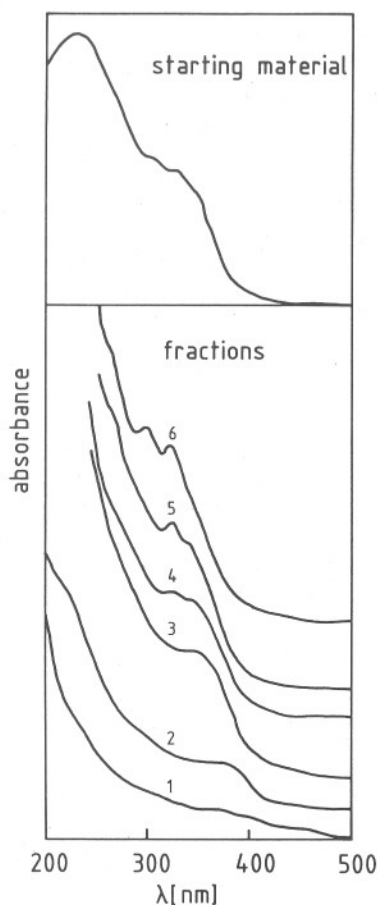


Fig. 1

Absorption spectrum of a Q-CdS sol (upper part) and of six fractions (lower part). The absorption spectra of the fractions are vertically shifted. The absorbance range, in which the spectra were taken was 0.1 for fractions 1 and 6, 0.5 for fractions 2, 3, and 4, and 0.3 for fraction 5

Various commercially available gels (sephadex, sepharose, sephacryl of different pore sizes) were tested as stationary phases. The best results were obtained with the combination of three sephacryl-gels of different pore-sizes as described in the experimental part. The upper part in Fig. 1 shows the absorption spectrum of a sol of Q-CdS which was used for the particle separation. The sol was prepared according to the method described previously [6].

$2 \cdot 10^{-4}$ M CdS was precipitated in the presence of $2 \cdot 10^{-4}$ M sodium hexametaphosphate by injecting the calculated amount of H_2S into a deaerated solution of $\text{Cd}(\text{ClO}_4)_2$ at pH = 9.8. The colloidal particles were brought into the solid state by removing the solvent in a rotor-vapor apparatus. The metaphosphate was also solidified and acted as protecting agent which prevented the small particles from coming into close contact. The almost colorless powder was stored in a refrigerator. The solution for gel chromatography was made by dissolving the powder at $(1 \text{ to } 2) \cdot 10^{-3}$ M. The spectrum in the upper part of Fig. 1 shows that the main absorption begins at about 420 nm, i.e. far below the wavelength of 515 nm where macrocrystalline CdS begins to absorb. The spectrum is weakly structured, i.e. shoulders or maxima in the range between 300 and 360 nm are present.

The lower part of Fig. 1 shows the absorption spectra of 6 fractions. The first fraction has an unstructured absorption spectrum beginning at 500 nm. The second fraction has a shoulder at 390 nm which is attributed to an exciton transition. This shoulder grows into a maximum and is shifted towards shorter wavelengths in the next fractions. Also note that maxima, which are present in a fraction, disappear or become less pronounced in the succeeding fractions, while new maxima at shorter wavelengths become more important. These findings clearly show that an enrichment of particles of different size had occurred in the various fractions.

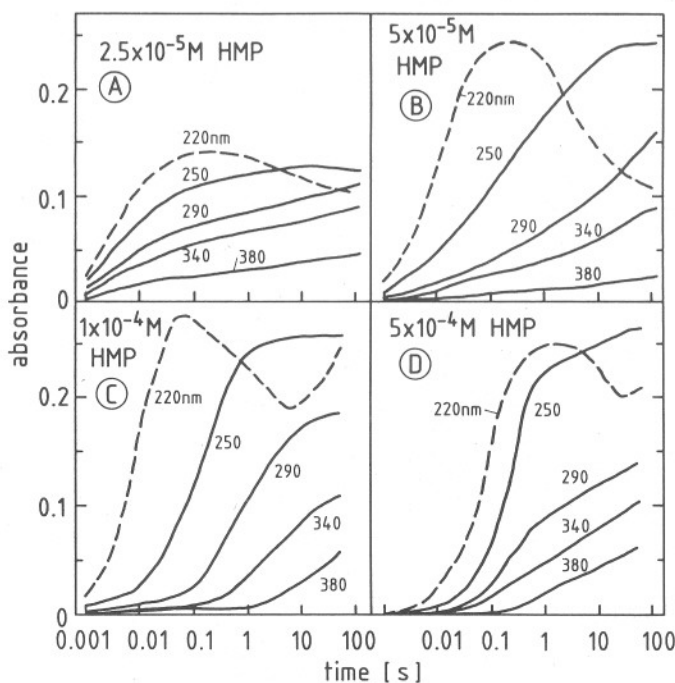


Fig. 2

Increase in absorbance as a function of time at various wavelengths. A, B, C, D: different concentrations of sodium hexametaphosphate (HMP). Mixed solution: $2 \cdot 10^{-4}$ M $\text{Cd}(\text{ClO}_4)_2$ and $1 \cdot 10^{-4}$ M NaSH pH 8

Stop Flow Experiments

Fig. 2 shows the changes in absorbance at various wavelengths for a mixed solution initially containing $2 \cdot 10^{-4}$ M $\text{Cd}(\text{ClO}_4)_2$, $1 \cdot 10^{-4}$ M NaSH and various concentrations of sodium hexametaphosphate (HMP). CdS is finally formed in a concentration of $1 \cdot 10^{-4}$ M, and excess Cd^{2+} ions remain. The full curves (wavelengths longer than 220 nm) give the increase in absorbance of the solution. The dashed curve for 220 nm is composed of the increase in absorbance due to CdS formed and the decrease in the absorbance of SH^- consumed (note that SH^- has an absorption maximum at 230 nm and recall that our measurement of light intensity I_0 occurred at a time when the solution had not yet reacted, i.e. when it still contained $1 \cdot 10^{-4}$ M SH^- ions). The fact that the 220 nm absorbance increases at the beginning of reaction shows

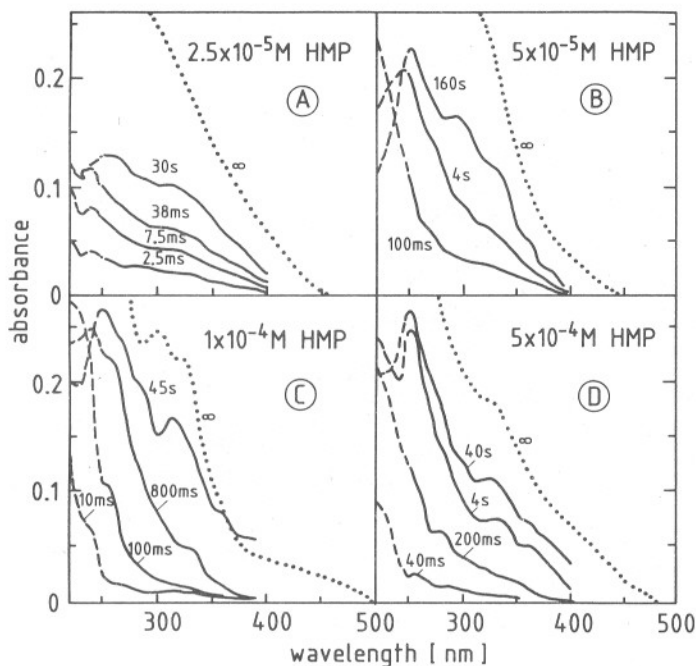


Fig. 3

Absorption spectrum at different times after mixing. A, B, C, D: as in Fig. 2

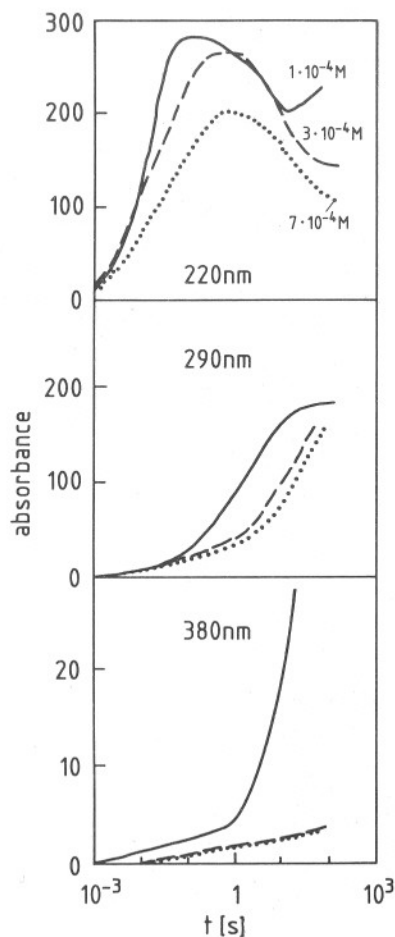


Fig. 4

Increase in absorbance at three wavelengths and different concentrations of excess Cd^{2+} ions $[\text{HMP}] = 1 \cdot 10^{-4} \text{ M}$, $[\text{SH}^-] = 2 \cdot 10^{-4} \text{ M}$

that the CdS particles produced have a stronger absorption at 220 nm than SH^- ions.

Fig. 3 shows the absorption spectrum of the solution at different times after mixing. The spectra were obtained from the absorbance vs. time curves which were recorded at every 10 nm. It is seen that the final spectrum of the solution (at $t = \infty$) exhibits the most pronounced maxima at $1 \cdot 10^{-4} \text{ M}$ hexametaphosphate. With increasing time the absorption starts at longer wavelengths and new maxima appear. These facts indicate that extremely small CdS particles are formed during 10^{-3} to 10^{-2} s after mixing. They absorb in the UV, and are at longer times transformed into larger particles, which absorb in the near UV or beginning of the visible.

The rate of the increase in absorbance is quite different at the various wavelengths and at different HMP concentrations. In the cases of the higher HMP concentrations (parts C and D in Fig. 2) pronounced induction periods are observed. The longer the wavelength, the longer is the induction period. This may be taken as an indication for a rather uniform growth of the particles. The absorption spectrum with several maxima develops most distinctly at $1 \cdot 10^{-4} \text{ M}$ HMP (Fig. 3C).

The dependence of the rate of CdS formation on the concentration of excess Cd^{2+} ions was investigated by recording the increase in absorbance of a solution containing $1 \cdot 10^{-4} \text{ M}$ HMP, $1 \cdot 10^{-4} \text{ M}$ NaSH and various amounts of $\text{Cd}(\text{ClO}_4)_2$ exceeding $1 \cdot 10^{-4} \text{ M}$. Fig. 4 shows the results. The initial rates of the increase in absorbance at 220 and 290 nm are little dependent on the excess Cd^{2+} concentration. However, at longer times the rate was always highest in the presence of $1 \cdot 10^{-4} \text{ M}$ excess Cd^{2+} . Experiments were also made with solutions which did not contain excess Cd^{2+} ions. The curves obtained were quite similar to the curves for $3 \cdot 10^{-4} \text{ M}$ excess Cd^{2+} . This shows that there exists an optimum concentration of excess Cd^{2+} at about $1 \cdot 10^{-4} \text{ M}$. The greatest difference was observed for the curves at 380 nm, where the build-up of the larger CdS particles occurred very slowly at the higher concentrations of Cd^{2+} . However, the final spectrum showed the most distinct structure under these conditions.

Experiments were also carried out with solutions which contained excess SH^- ions. SH^- ions were found to exert a much stronger influence on the rate of CdS formation at all wavelengths of observation than Cd^{2+} ions. With increasing SH^- concentration, the rate increased. However, the final spectra never showed any structure. In another series of experiments the concentration of all three solutes were varied, keeping the ratio of their concentrations constant. A typical solution contained $2 \cdot 10^{-4} \text{ M}$ Cd $(\text{ClO}_4)_2$, $1 \cdot 10^{-4} \text{ M}$ NaSH, and $1 \cdot 10^{-4} \text{ M}$ HMP. It was found that the rate of reaction increased with increasing concentrations.

Discussion

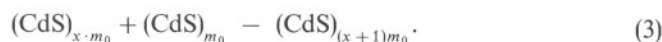
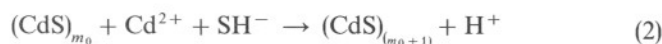
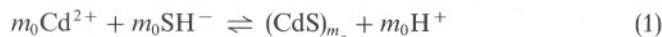
The results of the stop flow experiments are in agreement with the concept according to which the absorption of CdS particles shifts to longer wavelengths as they grow after the mixing of the Cd^{2+} and SH^- containing solutions. Certain concentration conditions exist where the spectrum develops maxima during the particle growth. These maxima are believed to result from particles of preferential sizes. The experiments on the exclusion chromatography of Q-CdS sols with structured absorption spectrum confirm our previously expressed view that the absorption maxima are caused by particles of different sizes [6].

Sodium hexametaphosphate (HMP) has a strong influence on both the rate of growth of the CdS particles and their final size distribution. At HMP concentrations lower than the Cd^{2+} ion concentration (Figs. 2A and B) the growth of absorption at all wavelengths is rather uniform, i.e. practically no induction periods are observed at the longer wavelengths. The particles obviously grow in a very broad size distribution even at short times after mixing. As the HMP concentration becomes comparable to the Cd^{2+}

concentration (Fig. 2C), the particles grow within a more narrow size distribution. These distributions contain maxima due to particles of preferential sizes. At HMP concentrations above the Cd^{2+} concentration (Fig. 2D), the differences in the induction periods become smaller and again the particles grow in a broader size distribution. Their absorption spectrum at the end of reaction is less structured.

Cd^{2+} ions are strongly bound to hexametaphosphate anions. This can be shown by polarography. When hexametaphosphate is stoichiometrically added to a Cd^{2+} solution, the wave of Cd^{2+} is suppressed. At a low HMP/ Cd^{2+} concentration ratio, a large percentage of the Cd^{2+} ions is free in solution (Figs. 2A and B). It seems that under these circumstances a mechanism of growth is operative which leads to broad size distributions during the reaction. When the HMP/ Cd^{2+} ratio is about 0.5, a large percentage of the Cd^{2+} ions is bound and present on the HMP matrix in a high local concentration. It seems that a uniform growth of the particles occurs under these conditions. At still higher HMP/ Cd^{2+} ratios (Fig. 2D), most of the Cd^{2+} ions will be bound, but they will be present on the matrix in lower local concentrations. This seems to lead to a lower rate of growth. Although HMP plays an important role, it should be mentioned that in other solvents HMP is not a prerequisite for obtaining colloids with structured absorption spectra. For example, when CdS is precipitated in alcohol at -78°C , a spectrum with several maxima is observed [6].

The precipitation mechanism recently proposed [6] did not distinguish between CdS formation in bulk solution and on the HMP matrix. In this mechanism, the following reactions were considered:



In the beginning very small primary CdS particles are formed, the size distribution of which is peaking at an agglomeration number m_0 . The solubility product of these particles probably is rather large. Eq. (2) describes the particles growth via Ostwald ripening, and Eq. (3) via combination. Particles with preferred agglomeration numbers are formed in the latter kind of growth ($x = \text{integer number}$). To obtain a structured size distribution, Ostwald ripening has to be prevented [6].

If a large excess of Cd^{2+} ions is present and the HMP/ Cd^{2+} ratio is small, particles will be formed almost exclusively in bulk solution. Ostwald ripening will be slow as the equilibrium of Eq. (1) is shifted to the right hand side. The $(\text{CdS})_{m_0}$ particles will be bound to the HMP matrix and combine there. This combination is a slow process, but leads to a colloid with a structured size distribution. With decreasing excess Cd^{2+} concentration, more and more CdS will directly be formed on the matrix by reaction of SH^- ions with bound Cd^{2+} ions, and this kind of precipitation does not favor the occurrence of a structured size distribution. However, the rate is greater than that at larger excesses of Cd^{2+} ions. Finally, when SH^- is present in excess (and the ratio HMP/ $\text{Cd}^{2+} > 0.5$; i.e. all Cd^{2+} ions are bound), CdS is exclusively precipitated on the matrix, and the size distribution during precipitation is now very broad. These considerations suggest that the best structured distributions are obtained when 1) the Cd^{2+} ions are present in excess, and 2) the concentration ratio of HMP to CdS formed is about 0.5.

The authors wish to thank Mrs. S. Podgurski for her assistance in the experiments on exclusive chromatography.

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(Eingegangen am 22. August 1985)

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