Photo-Chemistry of Colloidal Metal Sulfides
8. Photo-Physics of Extremely Small CdS Particles: Q-State CdS and Magic Agglomeration Numbers

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Extremely small CdS particles were prepared in propanol-2 solution at $-78\,°C$ and in aqueous solution in the presence of sodium hexameta-phosphate at room temperature. These colloids are colorless. Their UV absorption spectra exhibit several maxima. Aging of the colloids is accompanied by intensity variations in the absorption maxima and by a shift of the onset of absorption to longer wavelengths. These small CdS particles hardly possess semiconductor properties (Q-state CdS). A semi-classical treatment of the energies of an electron-hole pair in these particles yielded the wavelengths of their absorption spectra. At the small particle sizes used, the first excited state was reached by photon-absorption in the UV, and the second excited state was generally not reached at all. The various maxima in the absorption spectra are explained in terms of a size distribution of the colloids with preferential agglomeration numbers. Reasons for the formation of such a structured size distribution are given. The fluorescence and fluorescence excitation spectra of the small particles were also investigated. Particles below a certain size have only one broad fluorescence band at a much longer wavelengths than the onset of absorption. As the particle size increases, this band is shifted towards longer wavelengths, and finally an additional rather sharp band appears at the threshold of absorption. CdS colloids in the Q-state can be made which fluoresce as desired anywhere between the red and the blue. Also reported are the first experiments in which the preparation of Q-type CdS in the solid state is achieved by evaporating the solvent from the colloidal solutions.

Introduction

In the previous papers of this series, CdS and ZnS were found to fluoresce in the colloidal state, and it was further observed that these fluorescences could be quenched by solutes at low concentration, and that these colloids can act as catalysts for various photochemical reactions. In the last paper attention was drawn to the photo-physics of extremely small ZnS particles and it was pointed out that the particles lose their semiconductor properties as they become smaller and smaller [1]. Brus and coworkers [2 – 4] have made similar observations on CdS,

where significant changes in the optical absorption spectrum occurred at particle sizes below 5 nm.

In the present paper, various methods are reported for the preparation of extremely small and fairly stable CdS particles in solution and even in the solid state. The optical absorption spectra, the fluorescence spectra, and the fluorescence excitation spectra of these colloids are reported. A difficulty in the preparation of colloidal CdS by precipitation of Cd^{2+} by added H_2S consists of the fact that a certain size distribution will always be produced instead of a monodisperse system. A sur-

prising distribution however, was obtained in our experiments on the preparation of small CdS particles in alcohol solution at low temperature or in aqueous solution at room temperature in the presence of a complexing stabilizer. The distribution did not only possess one maximum (as it is the case for colloids of larger size), but had many maxima with about equal spacing of the agglomeration number m. This means that small clusters of CdS of a preferred agglomeration number m_0 are formed in the precipitation, and that the particles grow via the combination of these clusters leading to maxima in the size distribution at $N \cdot m_0$ (where $N = 1, 2, 3 \ldots$). Recognition of these various particles is possible, as they have different absorption and fluorescence spectra.

The reason for these differences in the photo-physical properties of the very small particles lies in the quantum mechanical effects on the electronic energy levels as the space is more and more restricted. In a macrocrystalline semiconductor, light absorption leads to an $e^- - h^+$ pair, as the electron is lifted from the valence into the conduction band (leaving the hole h^+ in the valence band). Slightly below the lower edge of the conduction band are the levels of the exciton, i.e. a state where the charge carriers do not move independently of each other. As the lowest exciton state is so close to the conduction band, thermal activation often leads to separated charge carriers from the exciton. When the semiconductor particle is very small, the electron in the conduction band feels the restriction in space (electron in a spherical box). Phenomenologically, the absorption coefficient becomes smaller than in the macrocrystalline material, while the light absorption practically still occurs at the band gap energy (as the exciton state of the material is not yet substantially affected). At still smaller particle size, the exciton state (which is more compact than an electron in the conduction band) is also influenced, and the beginning of absorption is drastically shifted towards higher photon energies. When this "Q-state"

of the material is reached (where Q stands for unusual quantum effects that lead to different physical or chemical properties of a material as compared to those of macropieces of the material), it seems unimportant whether one still regards the electronic properties of the material from the point of view of semiconductor structure (i.e. levels widely spread in space) or molecular structure (i.e. localized levels). The transition from semiconductor to polymolecular (and finally monomolecular) material will be a gradual one. Many inorganic materials should exist in the Q-state, although it may, in many cases, be difficult to find appropriate methods of preparation.

In the discussion of our experimental results, an approximation was used which is a little different from Brus' treatment [3]. As described in more detail in the appendix, we consider an electron in a spherical box of radius R assuming a positive charge (i.e. the positive hole to be located) in the center as a model for an exciton. The energy levels are determined by the electrostatic potential field for $r < R$ (r = distance from the center) and by the infinite potential at $r = R$. Fig. 1 shows calculated energy levels for various values of R. When R is infinite (a), one finds the various levels of the exciton which converge towards the lower edge of the conduction band, E_c, as ionization limit; for intermediate R values (b), a limited number of almost a equidistant levels exist near the energy of the conduction band (of the macrocrystal); for small R values (c), the first available electronic level is still near the energy E_c, but there is already a great distance to the second available level. For still smaller particles, the first electron level lies high above E_c (d). The particle sizes dealt with in this work corresponded to situations close to (c) and (d).

The extremely small particles have not been paid much attention to in conventional colloid chemistry, although colloid chemists use "seeds" for nucleation to produce large particles. It seems that a systematic investigation of seeds which fall into the transition range between semiconductor and molecular properties has never been carried out. Studies of this kind, i.e. in the modern world of the neglected dimensions (to refer to a famous saying of Wo. Ostwald) [5], should contribute not only to photo-physics and photo-chemistry but also to colloid chemistry itself.

Experimental

Preparation of Colloids

The following methods for the preparation of the various colloids should be followed literally as small alterations in the procedures may lead to significant changes in the properties of the colloids. Three colloids are described: "CdS-P" is a colloid produced in propanol-2 solution at low temperature; it should be mentioned that Brus has also used an organic solvent (acetonitrile) in his work on small CdS particles [4]. Note that the "CdS-P" colloid was made without a stabilizer. The two other colloids were prepared in aqueous solution at ambient temperatures. "CdS-HMP" designates the colloid which was obtained by precipitating CdS in the presence of sodium hexametaphosphate. The third colloid was made in a solution containing sodium hexametaphosphate as complexing agent and colloidal silicon dioxide as stabilizing agent: "CdS-HMP on carrier". The silicon dioxide was a commercial sample (Ludox SM-30 from Dupont; particle size: 7 nm).

It may also be recalled that the CdS colloid used in the previous work [6] was stabilized by another silicon dioxide colloid (Ludox HS-30; particle size: 13 nm). This colloid had particles of larger size than reported here.
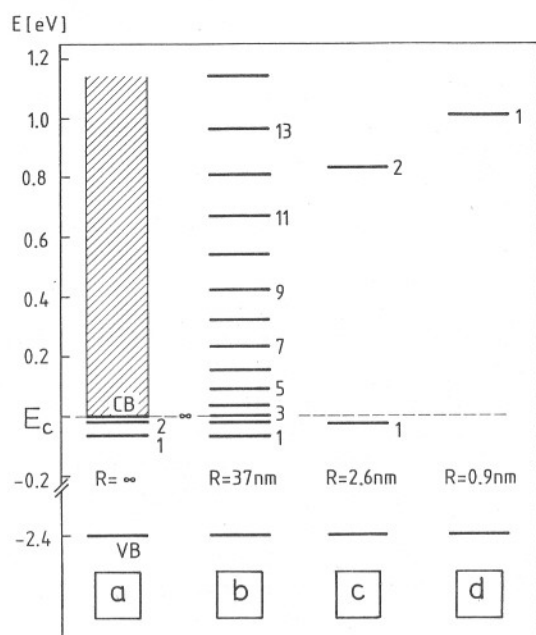

Fig. 1
Electronic energy levels in CdS particles of different radius R.
a: macrocrystalline material; b→d: decreasing particle size of Q-type CdS

"CdS-P" colloid: 420 mg $Cd(ClO_4)_2 \cdot 6 H_2O$ were dissolved in 1 ml water and added to 99 ml propanol-2. 2 ml of this stock solution were diluted with 98 ml propanol-2 and cooled to $-78°C$ in a 250 ml round bottom flask, to which a rubber septum was attached. 440 μl gaseous hydrogen sulfide were injected, the liquid being vigorously stirred. The $2 \cdot 10^{-4}$ M CdS solution was colorless and could be kept at room temperature for several weeks. Addition of 10 vol.-% of water made the solution turn yellow within minutes until yellow CdS finally precipitated. A few experiments were also made with a $1 \cdot 10^{-4}$ M CdS solution (containing $1 \cdot 10^{-4}$ M excess Cd^{2+}), which was obtained by adding only 220 μl H_2S gas to the $Cd(ClO_4)_2$ solution.

"CdS-HMP" colloid: Note that light and air were excluded during the preparation of this colloid. 100 ml of a solution containing $2 \cdot 10^{-4}$ M $Cd(ClO_4)_2$ and $1.5 \cdot 10^{-4}$ M $(NaPO_3)_6$ were bubbled with nitrogen for 1 h, then 0.4 ml of 0.1 M NaOH injected and the solution bubbled further. The pH of the solution was 9.6. The nitrogen stream was now interrupted and 220 μl H_2S gas injected, the solution vigorously shaken for a few seconds and bubbled with N_2 for 20 min. The pH of the solution was now 7.5. The colorless solution contained CdS at $1 \cdot 10^{-4}$ M and $1 \cdot 10^{-4}$ M excess Cd^{2+} ions. The solution was stable for weeks. It acquired a greenish and finally yellow color upon warming up to 80°C.

"CdS-HMP colloid on carrier": 440 μl H_2S was were injected into 100 ml of an aqueous, deaerated solution containing $2 \cdot 10^{-4}$ M $Cd(ClO_4)_2$, $5 \cdot 10^{-5}$ M $(NaPO_3)_6$, $6 \cdot 10^{-3}$ M SiO_2-colloid (Ludox HS-30, 1000 times diluted) and $2 \cdot 10^{-4}$ M NaOH. The solution was shaken and bubbled with nitrogen for 30 min. It contained the colloid at $2 \cdot 10^{-4}$ M without excess Cd^{2+} ions. The solution was colorless and stable for weeks.

Apparatus

UV-VIS spectra were recorded with a Shimadzu UV 240 double beam spectrophotometer with 2 nm slit width. Emission spectra were measured in the right angle position in a Shimadzu RF 540 fluorimeter. Fluorescence excitation spectra were obtained by scanning the excitation wavelength at a fixed emission wavelength. The excitation spectra were corrected for the spectral distribution of the excitation light intensity using the rhodamine B method (the stored spectra were divided by the excitation spectrum of rhodamine B (1% ethanediol) measured in the front face position at 630 nm). Fluorescence decay curves were obtained with an Edinburgh Instruments 199 single photon counting fluorescence spectrometer.

Results

Photo-Physics of CdS Stabilized by $(NaPO_3)_6$ and Colloidal SiO_2 in Water

Of the three colloids prepared, "CdS-HMP on carrier" had the largest particles. Fig. 2 shows the absorption spectrum. The onset of absorption is at 450 nm, i.e. far below the threshold of 515 nm of macrocrystalline CdS. Note that the CdS colloid used in the previous work [6] still started to absorb at 515 nm, although its absorbance at shorter wavelengths was much smaller than that of macrocrystalline CdS. A weak maximum is observed at 420 nm in Fig. 2; note that the
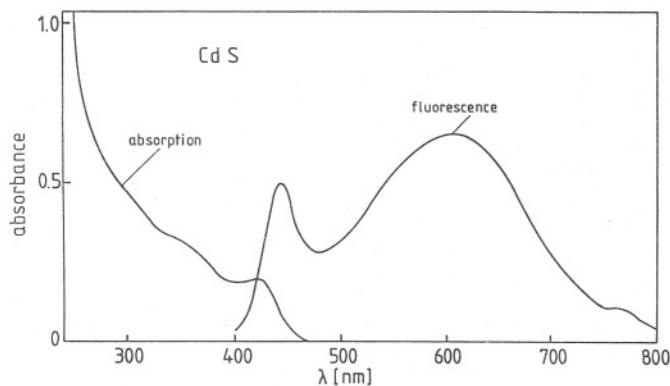
previously used CdS had a weak shoulder some 50 nm below the onset. By analogy with recent observations on ZnS and in agreement with Brus' view [4] we attribute the maximum to excitations to the exciton state. At shorter wavelengths in Fig. 2, the absorbance increases and a very weak shoulder appears around 350 nm.

The fluorescence spectrum contains three bands, i.e. a sharp one at 450 nm where the absorption of the colloid begins, a broad band from 450 to 800 nm peaking at 600 nm, and a weak band at 760 nm (at 760 nm, the sensitivity of our fluorimeter is low, the band therefore appears too weak). The shape of the fluorescence spectrum was not dependent on the wavelength of the exciting light.

Fig. 3 shows that the fluorescence at 540 nm decays within about 100 ns. This seems remarkable since extremely short decay times (<1 ns) were found in all the previous studies on the fluorescence of colloidal CdS [7, 8]. The fluorescence at 442 nm decays much faster than the 540 nm fluorescence. At 442 nm the process which produces the broad second fluorescence band also contributes to the measured fluorescence. One therefore has to conclude that the state, the decay of which produces the first fluorescence band, decays even faster than indicated by the curve at 442 nm in Fig. 3. The decay curves could not be fitted by first order kinetics, they are of multiexponential order as recently observed for the fluorescence of colloidal ZnS [1, 9].
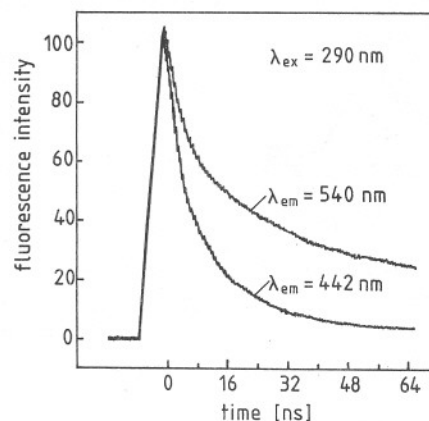
Fig. 3

Fluorescence intensity as a function of time at two wavelengths (colloid: "CdS-HMP on carrier"). The curves were normalized at time zero
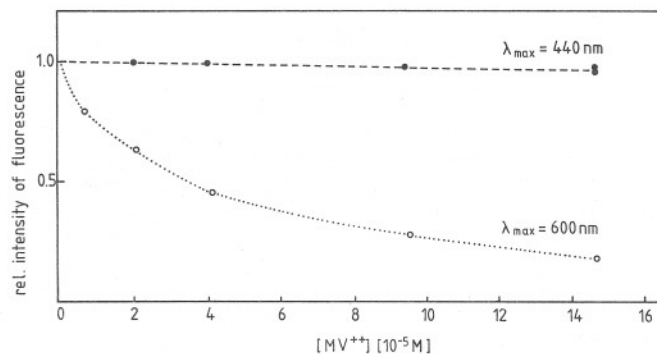
Fig. 4

Intensity of the fluorescence at 440 and 600 nm as a function of the concentration of added methyl viologen ("CdS-HMP colloid on carrier")

In the first paper of this series, methyl viologen (1,1'-dimethyl-4,4'-bispyridylium dichloride, MV^{2+}) was found to be a quencher of the fluorescence of colloidal CdS [6]. Quenching experiments with MV^{2+} have subsequently been carried out by other authors [10,11]. Fig. 4 shows that the fluorescence at 600 nm (second band) is very efficiently quenched by MV^{2+}. However, that of 440 nm was not quenched at all (it should be mentioned that the contribution at 440 nm of the second band was always subtracted). This finding corroborates the above conclusion about the short life time of the state which emits the fluorescence of the first band in Fig. 2.

Fig. 2

Spectra of absorption and fluorecence of a $2 \cdot 10^{-4}$ M colloid ("CdS-HMP on carrier")

Structured Spectra of CdS Stabilized by $(NaPO_3)_6$ in Water

The absorption spectrum of a freshly prepared "CdS-HMP" colloid is shown in Fig. 5a. The absorption begins at 410 nm, indicating that the particles of this colloid were much smaller than those of the above colloid stabilized with Ludox (Fig. 2). At shorter wavelengths, several maxima are seen, the one at 274 nm being the most pronounced. The fluorescence spectrum contains only one broad band peaking at 460 nm. The fluorescence exitation spectrum was taken at 500 and 630 nm (arrows). The excitation spectrum at 630 nm is not very structured, while that at 500 nm exhibits even more distinct maxima than the absorption spectrum. Note also that a strong maximum in the excitation spectrum does not always correspond to a strong maximum in the absorption spectrum. This unusual relation between absorption and fluorescence excitation is also illustrated by Fig. 6 where the fluorescence spectra are shown for two wavelengths of the exciting light. It can be seen that the position of the fluorescence band depends on the kind of excitation. These observations as well as the changes in the spectra occurring upon aging, which are described below, lead us to believe that the colloid of Fig. 5 contains particles of different size which have significantly different absorption and fluorescence properties.
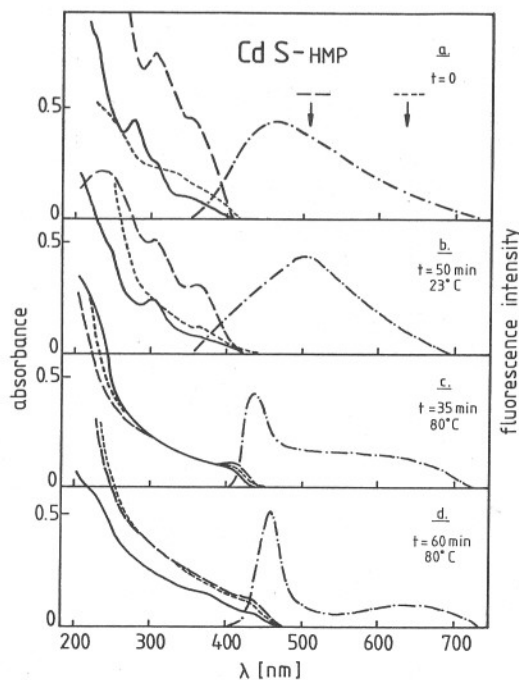
The spectral changes observed upon aging of the sol can be recognized from parts b–d of Fig. 5. The absorption starts at longer wavelenghts than in Fig. 5a indicating that the particles increased in size. All the maxima observed in Fig. 5a are still present in the absorption and 500 nm fluorescence excitation curves in Fig. 5b. However, the relative heights of the absorption maxima are changed, the tendency being an increase in relative height for the maxima at longer wavelengths. The heating procedure applied in Figs. 5c and d led to the disappearance of the structure in both the absorption and the 500 nm fluorescence excitation spectrum. In fact, the excitation spectra now have the same shape as the absorption spectra, which is the more usual case in photo-physics. On the other hand, a drastic change in the fluorescence spectrum is observed, since two bands appear now as was already observed for the fluorescence of larger CdS particles (Fig. 2).

Experiments were also carried out with solutions which contained twice the amount of $(NaPO_3)_6$. Under these conditions, even smaller particles were obtained. The colloidal solution first had a maximum at 206 nm. Upon aging at 50°C, the onset of absorption shifted to longer wavelengths, an additional maximum at 246 nm appeared, and further aging produced the maximum at 274 nm. However, when still higher $(NaPO_3)_6$ concentrations were applied, a yellow colloid of larger particle size was produced. The yellow colloid also appeared, when additional $(NaPO_3)_6$ was given to the solution of the colorless colloid. Addition of other salts, such as NaCl or Na_2SO_4, did not result in the conversion of the colorless to the yellow colloid.

Fig. 5
a: Absorption spectrum (———), fluorescence spectrum ($-\cdot-$), and fluorescence excitation spectra ($---$ at 500 nm; ----- at 620 nm) of a freshly prepared "CdS-HMP" colloid. b–d: spectra after aging and/or heating. Ordinate scale: arbitrary for all fluorescence spectra
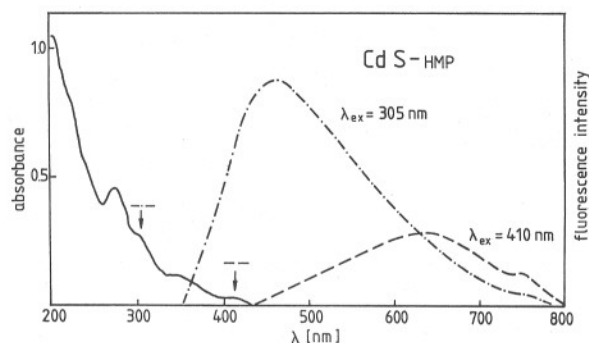
Table 1
Wavelengths of the observed absorption maxima of "CdS-HMP" and calculated agglomeration numbers (from Fig. 2A)

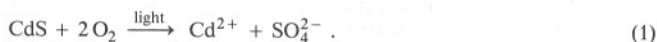| λ nm	m
206	12
246	18
274	24
302	32
324	40
342	48
360	56
370	64
381	72
395	84

In Table 1, the wavelengths of all the maxima are listed which were observed for "CdS-HMP" colloids, considering both freshly prepared and aged samples. The table also contains the agglomeration numbers of CdS particles which absorb at these wavelengths (using Fig. 2A of the appendix and assuming that the absorption is due to the excitation to the first excited state of the CdS particles, i. e. $n = 1$ in Fig. 2A). The mean difference m_0 between neighbouring agglomeration numbers is close to eight.

Photo-Physics and Photo-Anodic Dissolution of CdS in Propanol-2

The $1 \cdot 10^{-4}$ molar CdS sol had a structured absorption spectrum as long as it was kept at −78°C. The absorption began at 395 nm and maxima at 255, 275 and 305 nm were recorded. Upon warming up to room temperature, the maxima as well as the onset of absorption shifted to longer wavelengths until an absorption spectrum with only one distinct maximum at 370 nm was obtained.

The $2 \cdot 10^{-4}$ molar CdS sol had only one distinct maximum at 330 nm at −78°C. After warming up to room temperature, the onset of absorption was at 410 nm and the maximum at 370 nm. This spectrum is shown in Fig. 7, which also contains the spectra after various times of illumination of the solution. Further, the fluorescence spectra before and at the end of the illumination are shown.

Colloidal CdS is known to dissolve photo-anodically when it is illuminated in the presence of air [6]:

$$CdS + 2O_2 \xrightarrow{\text{light}} Cd^{2+} + SO_4^{2-} . \tag{1}$$

Fig. 6
Absorption spectrum and fluorescence spectra at two wavelengths of excitation ("CdS-HMP" colloid as in Fig. 5a)

As CdS is consumed, the intensity of the absorption spectrum decreases. However, it can also be seen that the shape of the spectrum changes. As the particles become smaller the onset of absorption shifts to shorter wavelengths and so does the absorption maximum. This effect has already been described for colloidal ZnS [1]. The fluorescence became stronger as a result of the illumination; this effect has already been observed for larger CdS particles [1]. The color of the fluorescence was yellow-orange at the beginning and green after the illumination in Fig. 7 (shift of the maximum of the fluorescence band from 520 to 500 nm). The fluorescence intensity was greater by several orders of magnitude than for the CdS colloid previously investigated [6]. In fact, the fluorescence could readily be seen in an only slightly darkened room. The quantum yield of fluorescence was $2 \cdot 10^{-2}$ at the end of the illumination experiment of Fig. 7.
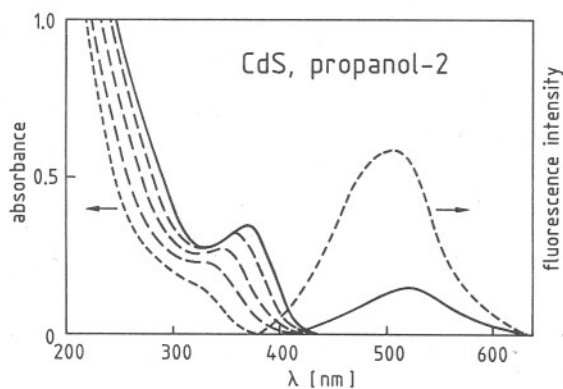

Fig. 7

Absorption and fluorescence spectra of CdS in propanol-2 at various times of illumination with 366 nm light (full line: before illumination; dashed lines: 1, 2, 5, and 22 min)

The photo-dissolution of CdS was quantitatively followed by determining the Cd^{2+} concentration with a polarograph. The sulfate ions were detected with an ion-chromatograph. At the beginning of the illumination, the quantum yield of reaction 1 was 0.03. A similar yield was previously reported for the photo-anodic dissolution in water [6]. It was further observed in the present studies that the quantum yield decreased with progressing illumination, or, in other words, with decreasing particle size. After 30% consumption of CdS, the quantum yield had already dropped to 0.01.

Table 2

Photochemical degradation of "CdS-P" colloid in aerated solution: CdS-concentration (from polarographic measurements) and wavelengths of absorption maximum at various times of illumination. The agglomeration number in the fourth row was calculated from the consumption of CdS, the one in the fifth row from the position of the absorption maximum

Illumination [min]	CdS [10^{-4} M]	λ_{max} [nm]	m from chemical conversion	m from absorption spectrum
0	2.0	372	65	65
1	1.8	350	52	52
2	1.7	340	47	47
5	1.6	335	44	45
22	1.3	330	42	43

Table 2 shows the agglomeration number m of the colloid at various times of illumination. This number was calculated from the polarographic measurements on the consumption of CdS and by taking $m = 65$ from Fig. 2A in the appendix for a particle absorbing at 372 nm. The table also contains m as calculated from the position of the maximum at the various illumination times, again using Fig. 2A. The agreement between the corresponding numbers is quite good.

The hydroperoxide $(CH_3)_2C(OH)OOH$ was found to be an important by-product of the photo-anodic dissolution of CdS. It was polarographically detected, the half wave potential vs. normal Ag/AgCl being

-1.3 V. The quantum yield of the formation of this peroxide is 0.4 molecules per photon absorbed, i.e. much greater than the quantum yield of the CdS dissolution. Further, it was found that the quantum yield became a little greater with progressing illumination, i.e. with decreasing particle size. At the end of the illumination in Fig. 7 the quantum yield was 0.6.

Colorless CdS in the Solid State (Solid Q-CdS)

As already mentioned above, the Q-state of CdS owes its unusual optical properties to the small size of the particles. The particles can be kept in solution for a long time. Certain procedures, however, such as the addition of water to a propanol-2 solution or heating, make the particles grow to form yellow CdS. To obtain Q-state CdS in the solid state by evaporation of the solvent from the colloidal solution, seemed to be a venture doomed to failure at first sight. However, a solid material of white or pale-yellow color was obtained by the following procedures. Both the solutions of CdS in propanol ("CdS-P") and in water ("CdS-HMP") were evaporated in a rotor-vapor apparatus at 40°C.

In order to obtain larger quantities of the solid material, higher concentrations of the colloid were used than given in the experimental part. In the case of the "CdS-P" colloid, a $5 \cdot 10^{-3}$ molar CdS solution was made at -78°C. When this solution was warmed up to room temperature, it had already acquired a weak yellow color, i.e. in contained a certain amount of larger CdS particles. These particles (about 10% of the CdS) were removed by illumination with light ($\lambda > 400$ nm) from a xenon lamp, taking advantage of the photo-anodic dissolution reaction 1. The solution became colorless and the colloid flocculated with a white color after a certain time. After evaporation of the solvent and drying under high vacuum a white powder was obtained. The powder could not be re-dissolved in propanol-2. Its fluorescence light was white with a yellow-orange tinge, which indicates that the fluorescence band stretched over the whole visible range of light. A few drops of water on the powder changed its color to deep yellow. The powder was not stable towards light. It developed first a reddish and then a gray color. At the same time, the characteristic smell of an organic thiol appeared. The solid contained not only CdS but also the cadmium sulfate which had been produced during the illumination of the solution prior to the evaporation of the solvent. An attempt was made to prepare the powder without the $CdSO_4$ component. Instead of evaporating the solvent, the coagulate produced by the illumination was separated by centrifugation, washed with propanol-2, and then dried under high vacuum. During the procedure the color turned yellow. It is therefore concluded that solid Q-state CdS can only be made in the presence of small amounts of another solid, such as $CdSO_4$, which protects the small CdS particles from touching each other.

In the experiments with "CdS-HMP", the colloid was prepared at a concentration five times higher than that given in the experimental part, using five times more $Cd(ClO_4)_2$ and $(NaPO_3)_6$. After evaporation a white powder with a yellow tinge was obtained. It could be re-dissolved in water to give a colloidal solution which had the same structured absorption spectrum as the solution before evaporation. The solid contained also the excess Cd^{2+} and hexametaphosphate. The powder had a beautiful blue fluorescence.

Further experiments with solid Q-state CdS are being carried out and will be reported elsewhere.

Discussion

Magic Agglomeration Numbers

The "CdS-HMP" colloid in water and the "CdS-P" colloid in propanol-2 at low temperature have absorption and fluorescence excitation spectra which exhibit several maxima. Most of these colloids consist of such small particles that the light absorption occurs only to the first excited state in the wavelength range investigated (corresponding to case d in Fig. 1*)). The
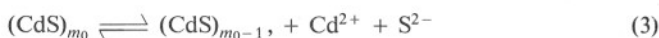
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*) In the case of larger particles which started to absorb at 480 nm, a shoulder was observed at 230 nm which possibly has to be attributed to the excitation to the second excited state.

structured absorption spectra can only be understood if one postulates a structured size distribution of the colloids. As the particles of different size have different absorption and fluorescence behaviour, the existence of particles of preferential size, i.e. of magic agglomeration number, can be recognized by optical measurements. Moreover, from the observed absorption maxima, which are listed in Table 1, we conclude that the magic agglomeration numbers are integral multiples N of a base number m_0, and it seems from the table that $m_0 = 8$.

Magic agglomeration numbers – as far as we know – have never been postulated to exist in the size distribution of a colloid. In fact, one would hardly expect such an effect for a colloid where the mean agglomeration number is much larger than m_0. However, for the very small particles of our colloids the mean agglomeration number is not so drastically different from m_0, N hardly exceeding 10. A colloid with structured size distribution would be formed if the ratio of the rates of nucleation to growth was very large. This would lead to a colloid with an initial size distribution peaking at a small agglomeration number m_0:

$$m_0 Cd^{2+} + m_0 S^{2-} \longrightarrow (CdS)_{m_0}. \qquad (2)$$
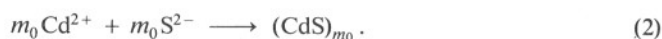
Further growth of the particles occurs via Ostwald ripening:

$$(CdS)_{m_0} \rightleftharpoons (CdS)_{m_0-1}, + Cd^{2+} + S^{2-} \qquad (3)$$

$$(CdS)_{m_0} + Cd^{2+} + S^{2-} \longrightarrow (CdS)_{m_0+1} \qquad (4)$$

or via combination of the initially formed particles:

$$2(CdS)_{m_0} \longrightarrow (CdS)_{2m_0} \longrightarrow . \qquad (5)$$
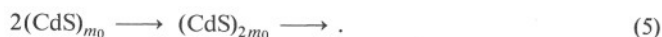
The growth by Ostwald ripening would not lead to a structured size distribution, while in the growth by combination there would be a preservation of the most abundant initial size m_0 in the form of integer multiples. Ostwald ripening is suppressed by using an organic solvent where the solubility product of CdS is very low. Lower temperatures are also favorable as the ratio of the rates of nucleation to growth is large under these conditions. This explains why the colloid produced in propanol-2 at $-78°C$ had a structured absorption spectrum. Added water catalyzed the particle growth as the larger solubility product of CdS in this solvent enabled the particles to undergo fast Ostwald ripening.

However, even in water it was possible to prepare small particles with a structured spectrum (Fig. 5a), provided that $(NaPO_3)_6$ was present. The hexametaphosphate influences the colloid in an intricate manner. Too large or too small concentrations of $(NaPO_3)_6$ lead to yellow CdS. Colorless colloid will only be obtained if the concentration ratio of excess Cd^{2+} to $(PO_3)_6^{6-}$ does not deviate much from two. The binding of Cd^{2+} ions on hexametaphosphate may play an important role. This effect can readily be shown to exist by polarography. When $1.5 \cdot 10^{-4}$ M hexametaphosphate is added to a $2 \cdot 10^{-4}$ M Cd^{2+} solution, the polarographic wave of Cd^{2+} is decreased to 25% of its initial value. As no rapid Ostwald ripening of the CdS particles is observed in the presence of hexametaphosphate, it must be concluded that this stabilizer decreases the solubility product of the CdS particles. This can only be understood in terms of a strong complex formed between CdS and $(PO_3)_6^{6-}$ anions.

The base agglomeration number of $m_0 = 8$ possibly corresponds to a structure of outstanding stability. It can easily be shown that an $m_0 = 8$ structure can be built in which all eight Cd^{2+} and S^{2-} ions are members of rings in a basically cubic structure. Only half of the ions are coordinatively twice unsaturated in this structure, no ions with threefold unsaturation being present. All possible structures with agglomeration numbers below and above eight contain a larger percentage of ions with higher coordinative unsaturation. The integral multiples of 8 also have a great degree of coordinative saturation of the constituent ions.

Fluorescence of Q-State CdS

As mentioned in the introduction, the unusual quantum mechanical effects due to the small size of the particles can produce significant changes in the photo-physical and photochemical properties of the material. The changes in the fluorescence behavior are quite typical.

Very small particles (size smaller than the dimension of an exciton in the macrocrystalline material) have a broad fluorescence band peaking at a wavelength longer than that of the onset of absorption. For example, the colloid in Fig. 5a emits light around 460 nm, the onset of absorption being at 410 nm. With decreasing particle size, both the onset of absorption and the fluorescence band are shifted to shorter wavelengths. For example, the yellow-orange fluorescence ($\lambda_{max} = 520$ nm) of the colloid in Fig. 7 turned into a green fluorescence ($\lambda_{max} = 500$ nm) as the particles became smaller. It is possible to prepare Q-state CdS of different particle size, to obtain a material which fluoresces as desired anywhere between blue and red. This fluorescence is attributed to the recombination of trapped electrons with positive holes, traps of different energies being involved. A more detailed description of this kind of recombination fluorescence has recently been given for colloidal ZnS [1].

At particle sizes which are comparable to the dimensions of an exciton in the macro-crystalline material, one observes a rather sharp fluorescence band at the beginning of the light absorption besides the broad band peaking at longer wavelength. Typical examples are shown by Fig. 5c and d, and Fig. 2. The time resolved fluorescence experiments in Fig. 3 and the quenching experiments in Fig. 4 showed that the lifetime of the state, which produces the fluorescence band at shorter wavelengths, is much shorter than the lifetime of the recombination of trapped electrons and holes which produces the fluorescence band at longer wavelengths. The emission at shorter wavelengths is attributed to a localized excited state of the CdS particles which, at larger particle sizes, turns into the state which is usually designated as exciton.

Absorption of Q-State CdS

The calculations of the energy levels in CdS particles of different size were made using a rather simple model (see appendix). All the experimental observations can be explained by these calculations. In the previous studies, it was pointed out

that CdS particles of about 3 nm diameter*) start to absorb close to the photon energy of 515 nm, which corresponds to the band gap energy of macro-crystalline CdS [6]. The curve for $n = 1$ in Fig. 2A of the appendix is in agreement with this observation. Further, it was found that the absorption at shorter wavelengths increased much more slowly than for a macropiece of CdS [6]. A look at Figs. 1b and c, where levels in particles of similar size are shown, makes one realize that there is little density of states at greater energies, i.e. the absorption coefficient for optical transitions from the valence band to the upper states is drastically decreased. Brus has already drawn attention to this fact [3, 4].

Very small particles, as were used in the present work start to absorb at photon energies appreciably higher than 2.4 eV (the band gap energy of ordinary CdS). In the extreme case, there was no absorption in the visible (Fig. 5a and b, Fig. 2) which means that the cadmium sulfide was colorless. The calculations, as represented by Fig. 1c and d, show that the second excited state of such particles lies very high, generally at energies greater than the photon energies between 200 and 600 nm, i.e. the range in which our absorption spectra were taken. Under these circumstances, it does not make sense to continue to talk about the existence of a conduction band. In our calculations, only Coulomb effects and the "particle in the box" effect were taken into account. As the particles become oligomers of low agglomeration number, this kind of calculation cannot be correct anymore as structural effects of the CdS molecule are not taken into account. It would be highly desirable to find a way of calculating the electronic levels in oligomeric CdS particles by an atomic orbital method.

The degradation experiment described by Table 2 allowed one to compare agglomeration numbers calculated from the spectrum of CdS with the numbers calculated from the measurement of chemical conversion. The fair agreement between these numbers encourages us to believe that our calculations are a reasonable approximation for the quantitative discussion of the effects observed. On this basis, we attribute the maxima in the structured absorption spectra of small particles (Fig. 5a and b) to a structured size distribution, as each particle size should be represented by only one maximum (corresponding to the transition to the first excited state) in the absorption spectra of the colloid. The maxima did not appear at random in the various colloids, but at rather distinct wavelengths which are shown in Table 1. The corresponding agglomeration numbers form a series with a practically constant difference between neighbouring members.

Solid Q-State CdS

It is due to the quantum mechanical nature of the unusual properties of the extremely small CdS particles that these properties should disappear when the particles are so densely packed in the solid state that they touch each other. Pure Q-state CdS, therefore, cannot be expected to exist in the solid state. However, solid samples were obtained by evaporation of the solvent from aqueous or alcoholic sols. In both cases, the

*) The value of 3 nm is a lower limit for the size of the previously used CdS particles as it must be concluded from electron microscopic pictures that several particles often stuck together. A larger "effective" diameter of the particles must, therefore, be considered.

solid contained small amounts of other material present in the solution, in which the small CdS particles were embedded.

In the case of the "CdS-HMP" colloid, hexametaphosphate complexes the particles and keeps them apart from each other after evaporation of the aqueous solvent [2]. In the CdS-hexametaphosphate complex, the ion product of CdS is strongly decreased, as pointed out above. Moreover, the complex is water soluble which explains the fact that the solid material could be re-dissolved.

In the case of the solid material obtained from the propanol-2 solution one must assume that $CdSO_4$ was the protecting stabilizer, as mentioned above. The solid material must still have contained some solvent molecules after drying under high vacuum. The photo-sensitivity of the material can only be understood in this way. (It may be noticed that the solid material from aqueous solutions containing hexametaphosphate did not decompose under light). As is discussed below, CdS oxidizes propanol-2 under illumination as positive holes react with the alcohol. The remaining electrons form cadmium metal which turns the color of the white powder to gray. Such photo-cathodic effects have already been described for CdS sols [12]. The formation of an organic sulfur compound in the illumination of solid "CdS-P" can also only be understood by assuming that some propanol-2 was retained in the solid.

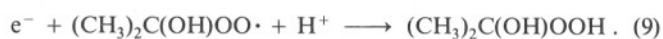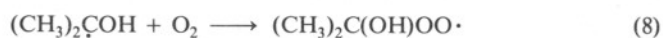## Photo-Anodic Dissolution and Photo-Catalytic Action of Q-CdS in Propanol-2

The present paper is concerned with the photo-physical properties of extremely small CdS particles, chemical effects will be discussed elsewhere. Only two reactions have been described in the present work: the photo-anodic dissolution of the "CdS-P" colloid in aerated solution and the formation of the organic hydroperoxide $(CH_3)_2C(OH)COOH$.

The quantum yield of the photo-dissolution (Eq. (1)) decreased with particle size, i.e. the CdS particles become more stable with decreasing size. In the experiment of Fig. 7 the quantum yield of CdS consumption was 0.03 at the beginning and 0.01 at the end. The reason for this decrease in the rate of dissolution may lie in an enhanced rate of competing processes such as the oxidation of the solvent or the fluorescence.

Simultaneously with the photo-dissolution, the solvent was oxidized. The yield of the hydroperoxide was initially 0.4 molecules per photon absorbed and 0.6 towards the end of the illumination. A mechanism is postulated in which the oxidation of propanol-2 by positive holes is the first step which occurs with a great quantum efficiency:

$$CdS \xrightarrow{\text{light}} CdS(e^- + h^+) \tag{6}$$

$$h^+ + (CH_3)_2CH(OH) \longrightarrow H^+ + (CH_3)_2\overset{\cdot}{C}OH . \tag{7}$$

The one-hole oxidation mechanism of propanol-2 has previously been investigated in more detail for colloidal ZnS [13]. In the presence of oxygen, the 1-hydroxy-1-methyl ethyl radical forms the peroxide:

$$(CH_3)_2\overset{\cdot}{C}OH + O_2 \longrightarrow (CH_3)_2C(OH)OO\cdot \tag{8}$$

$$e^- + (CH_3)_2C(OH)OO\cdot + H^+ \longrightarrow (CH_3)_2C(OH)OOH . \tag{9}$$

CdS acts as a sensitizer for the oxidation of propanol-2, and the photo-anodic dissolution of CdS is only a side reaction. One could argue that the oxidation of propanol-2 occurred in a chain reaction, i.e. the initiating step 7 did not occur with the great quantum yield of 0.4 to 0.6 but with a much smaller one. In order to check this possibility, a radiation chemical experiment was carried out. Aerated propanol-2 was γ-irradiated at a dose rate which produced the hydroperoxide at the same rate as in the photo experiment with CdS as sensitizer. The advantage of using γ-rays for the initiation of a chain reaction lies in the fact that the yield of radical production is known. The chain length can therefore readily be calculated from the yield of the product of the chain reaction. About seven radicals are formed in the radiolysis of propanol-2 per 100 eV of absorbed radiation energy.

Ten molecules of the hydroperoxide were formed per 100 eV. Therefore, it can be concluded that practically no chain reaction occurred under our illumination conditions. The quantum yield of 0.4 to 0.6 for reaction 7 is quite remarkable from the point of view that the upper edge of the valence band in CdS is at a potential of 1.8 to 1.5 V on the electrochemical energy scale (depending on the surface nature of the CdS, which is determined by the pH) and that the one-hole oxidation potential of propanol-2 is close to 1.8 V [13]. As a certain driving force for reaction 7 is required to make the process fast enough to compete with fluorescence or radiationless recombination of the $e^- + h^+$ pair, one must suspect that the positive hole is located at a more positive potential in Q-state CdS than in the macrocrystalline material. This question and other chemical reactions will be dealt with later.

Final Remarks

The investigation of the transition from semiconductor to molecules of a material leads one to a state of matter (Q-state) which has yet little been studied. The difficulty lies mainly in the preparation of the small particles. While a lot of research on small clusters in the gas phase using beam methods and in solid matrices is being carried out, little attention has been paid to small colloidal particles. In the present paper the optical absorption and fluorescence properties of extremely small CdS particles have been described. These properties are ruled by quantum mechanical restrictions due to the small space available for the charge carriers, which are produced by light absorption. The photo-catalytic properties of these particles still have to be investigated. It was also possible for the first time to bring the small particles from the colloidal solution into the solid state and then redissolve them without loss of the Q-state properties.

In the field of micro-electronics [14–17], semiconducting systems of low dimensionality are more and more frequently used as the size of the chips is decreased. Quantum mechanical effects in one dimension, i.e. the thickness of the semiconductor layer, have been observed, which may even be used to change the properties of a semiconductor, such as its band gap, in a desired manner. The studies on the three-dimensional quantum effects occurring in the extremely small colloidal particles should complement the observations made in semiconductor electronics.

Appendix

Eigenvalues of an exciton were estimated by the JWKB formula, assuming the positive charge localized in the center of the particle. The semiclassical quantum condition is (J = phase integral)

$$J = \int_{r_1}^{r_2} \frac{[2\mu^*(E - V(r))]^{1/2}}{\hbar} dr = (N + \tfrac{1}{2})\pi \quad (1A)$$

where μ^* is the effective reduced mass, r the radius vector and $N = 0, 1, 2, 3\ldots$. Using a one-dimensional electrostatic potential, the effective Coulomb potential can be written as

$$V(r) = -\frac{e^2}{\varepsilon r} + \frac{\hbar^2(l + 1/2)^2}{2\mu^* r^2} \quad (2A)$$

where ε is the dielectric constant of the medium and l the quantum number of angular momentum. Note that $V(r) = \infty$ for $r = 0$. r_1 and r_2 are the roots of $V(r) = E$. By expressing E in reduced Rydberg units $\mu^* e^4/2\hbar^2\varepsilon^2$ and r in units of reduced Bohr's radius $\varepsilon\hbar^2/\mu^* e^2$ one obtains for the phase integral

$$J = \int_{r_1}^{r_2} \left(E + \frac{2}{r} - \frac{(l + 1/2)^2}{r^2} \right)^{1/2} dr . \quad (3A)$$

Let $r = 1/y$, $Y = 1/R$, where R is the particle radius, and $y_{1/2} = [1 \mp (1 + E(l + 1/2)^2]^{1/2}/(l + 1/2)^2$ where y_2 is the larger root of $E + 2y - (l + 1/2)^2 y^2 = 0$.

With the integrals

$$I_1 = \int_Y^{y_2} \frac{dy}{y[E + 2y - (l + 1/2)^2 y^2]^{1/2}} \quad (4A)$$

and

$$I_2 = \int_Y^{y_2} \frac{dy}{[E + 2y - (l + 1/2)^2 y^2]^{1/2}} \quad (5A)$$

the phase integral J can be written as

$$J = \frac{[E + 2Y - (l + 1/2)^2 Y^2]^{1/2}}{Y} + I_1 - (l + 1/2)^2 I_2 \quad (6A)$$

and be solved in a close form.

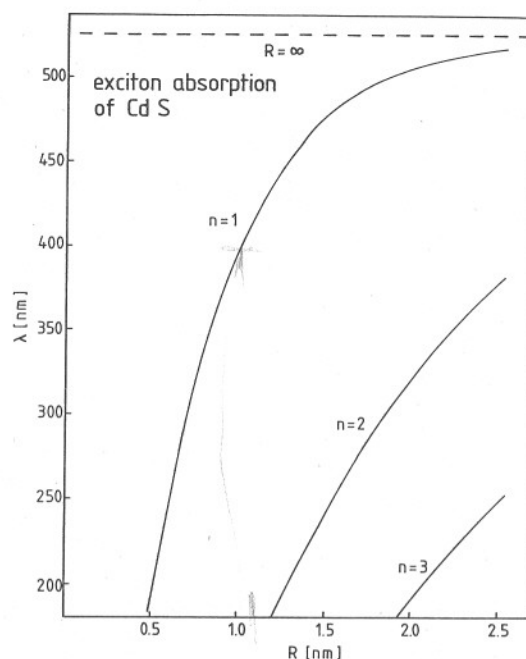The spacial restriction in the case of small colloidal particles was taken care of as follows:

Fig. 1A
Wavelength of excitation to the first three excited states ($n = 1, 2$, and 3) as a function of the radius R of the CdS particle
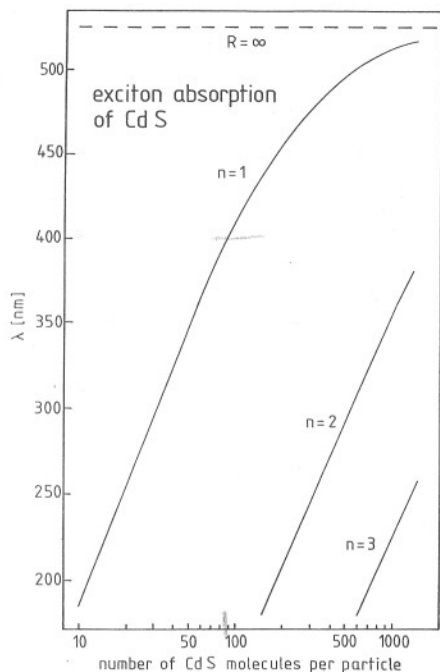
Fig. 2A
Wavelength of absorption as a function of the agglomeration number
of a CdS particle

Let the particle radius $R = 1/Y_R$. The integration limit Y was taken as y_1 for $1/Y_R \geq 1/y_1$ (i. e. the eigenstate is dominated by the Coulomb potential and is not influenced by the particle size) and taken as Y_R for $1/Y_R < 1/y_1$ (i. e the energy levels are mostly ruled by the infinite barrier at $r = R$). Solutions of J were sought by putting $l = 0$ (spherical orbitals), choosing Y_R, picking a trial E, then computing J, and checking whether the condition $J = (N + 1/2)\pi$ was fulfilled. $\varepsilon = 5.6$ and $\mu^* = 0.154$ was used, the volume of one CdS molecule was taken as $4.97 \cdot 10^{-23}$ cm^3. Figs. 1A and 2A show the calculated wavelengths for optical transitions to the first, second, and third excited state as func-

tions of the particle radius and of the number of CdS molecules per particle. The effects are not so pronounced as in Brus' calculations, which overestimate the shifts for smaller diameters [2 – 4].

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