Photochemistry of Semiconductor Colloids.
17. Strong luminescing CdS and CdS-Ag$_2$S Particles

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The luminescence of colloidal CdS in solutions containing sodium polyphosphate as stabilizer is activated by the addition of either Ag(ClO$_4$) or colloidal Ag$_2$S. The degree of activation depends on how strongly the CdS and Ag$_2$S particles are attached to each other, and this attachment is controlled by the concentration of polyphosphate and added divalent metal ions which bind to polyphosphate. The CdS fluorescence in these solutions can be excited by light of wavelengths longer than the wavelength of the absorption edge of CdS. The results are explained in terms of an interfacial region in which anion vacancies and incorporated silver centers, which deliver electrons into the conduction band of CdS upon illumination with photon energies less than the bandgap energy of CdS, are present. The preparation of Q-CdS sols which fluoresce with quantum yields close to 100% is also described. Strong fluorescence occurs when defect sites, at which radiationless recombination takes place, are blocked.

Introduction

In the first paper of this series it was reported that small amounts of Ag$^+$ ions in colloidal CdS particles strongly promote the luminescence of the particles without shifting the wavelength of the emitted light [1]. This effect is described in more detail in the present paper. Colloidal CdS solutions containing silver ions were prepared in three ways: 1) Co-precipitation of Cd^{2+} and Ag$^+$ ions with NaSH in the presence of polyphosphate as stabilizer, 2) Addition of Ag$^+$ ions to a CdS solution, and 3) Mixing of colloids of CdS and Ag$_2$S. It soon became evident that the polyphosphate stabilizer plays an important role, which strongly complexes CdS particles [2, 3]. In the equilibrium

$$(CdS)_n + PP \rightleftharpoons (CdS)_n\text{-}PP \qquad (1)$$

where (CdS)$_n$ is a particle of agglomeration number n and PP a polyphosphate molecule, particles of different degrees of complexation exist. The equilibrium can be shifted by adding metal ions, such as Cd^{2+}, Mg^{2+}, Ba^{2+} or Sr^{2+}, which strongly bind to polyphosphate [4—6]. Addition of these ions leads to a gradual detachment of the CdS particles from the polyphosphate chains and in the extreme case to flocculation.

Ag$^+$ containing CdS particles may act as chemical catalysts. Reber and Rusek [7] recently reported that platinized CdS powders, which are inactive with respect to H$_2$ formation upon illumination, can be activated by modifying their surface with silver ions. The activation was attributed to the formation of a heterojunction between CdS and Ag$_2$S working as a hole transfer catalyst. It was also observed that the fluorescence of CdS was quenched by Ag$^+$ ions, and that the spectral response for H$_2$ formation was extended to wavelengths up to about 600 nm where CdS itself does not absorb.

The preparation of CdS sols, which fluoresce with quantum yields close to 100%, is also reported. The composition of these sols (excess Cd^{2+} ions, polyphosphate concentration, pH and kind of solvent) is rather critical although the effect of the various components of such solutions is not fully understood. Nevertheless, some hypothetical explanations, which may lead in further studies, are given.

Experimental

Two kinds of CdS colloids were used. In most experiments, yellow-green CdS was used with a mean particle diameter of 2.7 nm. It was made by adding the stoichiometric amount of NaSH solution to a solution of $2 \cdot 10^{-4}$ M Cd(ClO$_4$)$_2$ and sodium hexametaphosphate, Na$_6$(PO$_3$)$_6$. The other sample was colorless Q-CdS (extremely small particles showing size quantization effects) prepared as described previously [2]. A solution of $2 \cdot 10^{-4}$ M Cd(ClO$_4$)$_2$ and Na$_6$(PO$_3$)$_6$ was deaerated by bubbling with argon and then half the stoichiometric amount of H$_2$S was injected. The pH of the solution was 8 to 9; it was adjusted with NaOH before the precipitation of CdS. The sodium hexametaphosphate was a commercial sample (Riedel de Haën) which, however, consisted mainly of polyphosphates with chain lengths up to 450. The polyphosphate molarities
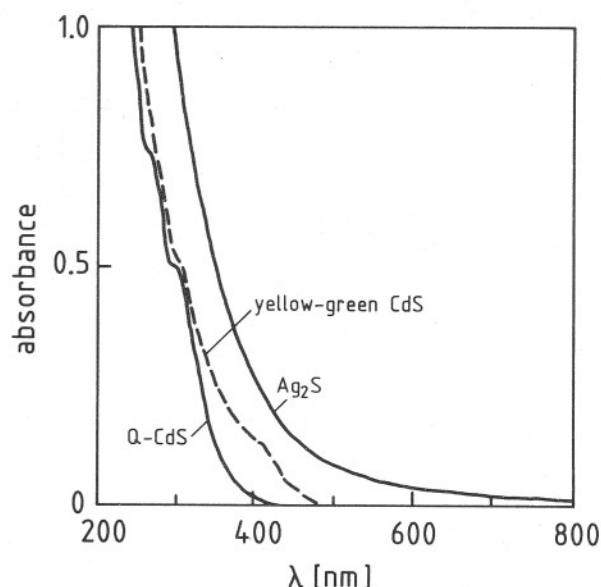

Fig. 1
Absorption spectra of CdS, Q-CdS, and an Ag$_2$S sol obtained by reaction of Q-CdS with silver ions. Concentration: $2 \cdot 10^{-4}$ M

are given with respect to the formula $Na_6(PO_3)_6$. In a few experiments polysilicate was applied as stabilizer using a commercial waterglass sample (Merck).

The absorption spectra of the two CdS samples are shown in Fig. 1. The figure also contains the spectrum of an Ag_2S sol of extremely small particle size. Such a sol cannot be prepared by adding NaSH or H_2S to a solution of $AgClO_4$ and polyphosphate as this procedure leads to larger particles. It was found that addition of the stoichiometric amount of Ag^+ ions to a sol of Q-CdS produced Ag_2S particles of small size:

$$2n\,Ag^+ + (CdS)_n \rightarrow (Ag_2S)_n + n\,Cd^{2+} \; . \qquad (2)$$
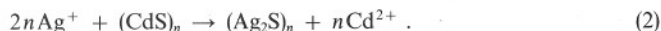
This reaction takes place within seconds.

The spectra of solutions containing both CdS and Ag_2S are superpositions of the spectra of the single components regardless of whether they were prepared according to the above methods 1, 2 or 3. Although only 1 weight % Ag_2S is soluble in the CdS lattice [8], in most of the experiments very much higher silver percentages were applied, i.e. the largest part of the silver is present in the form of an Ag_2S phase, and the various optical effects depend on the way in which this phase is attached to the CdS phase.

Quantum yields were determined by comparing the area of the fluorescence band with that of standard compounds (rhodamine B, fluorescein, cumarin-2 in methanol) which are known to fluoresce with almost 100% yield.

The excitation spectra were corrected for the varying intensity with wavelength of the exciting light using a 1% solution of pyridin-2, LC 7300 laser dye (Lambda-chrome) in methanol as a quantum counter. The advantage of this dye as compared to the commonly used Rhodamine-B dye is the long emission wavelength of 730 nm which allows one to correct in an extended wavelength range.
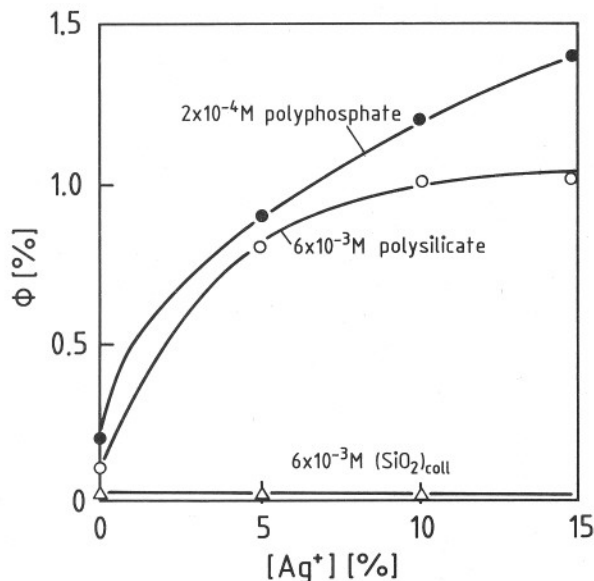

Fig. 2
Quantum yield of fluorescence of CdS on various carriers as a function of the concentration of added silver ions. Excitation of CdS with 420 nm light. The Ag^+ concentration is given as percent of the equivalent CdS concentration, which was $2 \cdot 10^{-4}$ M

Results

Different Stabilizers

Fig. 2 illustrates the strong effect which the stabilizer exerts on the quantum yield of the fluorescence of CdS solutions containing Ag^+ ions. The quantum yield is plotted here as a function of the concentration of added $Ag(ClO)_4$. The Ag^+ concentration is given in percent of the equivalent CdS concentration which was $2 \cdot 10^{-4}$ M (i.e. 100% Ag^+ is equal to $4 \cdot 10^{-4}$ M Ag^+). It is recognized that

Ag^+ ions increase the intensity of fluorescence in solutions containing polyphosphate or polysilicate as stabilizer, while they decrease the yield in solutions containing colloidal silicon dioxide (Ludox HS30 from Dupont).
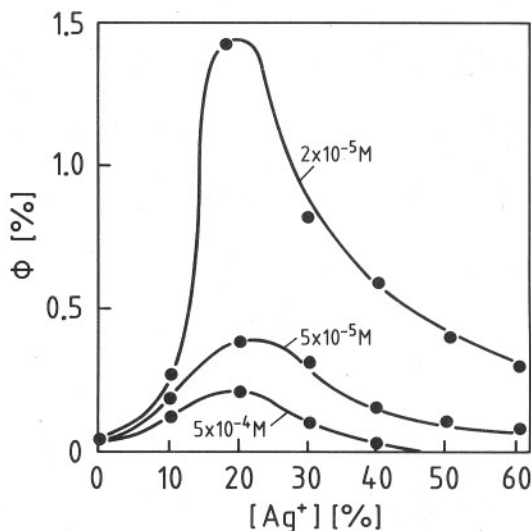

Fig. 3
Fluorescence quantum yield as a function of the concentration of added $AgNO_3$. The solutions contained $2 \cdot 10^{-4}$ M CdS and polyphosphate at various concentrations. The Ag^+ concentration is expressed in percent of the equivalent CdS concentration

CdS Colloids with Subsequent Addition of Silver

Different polyphosphate concentrations were used in the preparation of the $2 \cdot 10^{-4}$ M CdS solutions of Fig. 3. The solutions were made by adding different amounts of polyphosphate to a stock solution of $2 \cdot 10^{-4}$ M CdS and $2 \cdot 10^{-5}$ M polyphosphate. Silver ions were added afterwards and the quantum yield of fluorescence was determined. The yield passes through a maximum value at 20% Ag^+. With decreasing polyphosphate concentration the fluorescence yield becomes greater. It is important to note that the order in which polyphosphate and Ag^+ ions are added to the solution cannot be reversed. For example when the high polyphosphate concentration of $5 \cdot 10^{-4}$ M was established by adding $4.8 \cdot 10^{-4}$ M of the stabilizer to the strongly luminescing solution of $2 \cdot 10^{-5}$ M polyphosphate and 20% Ag^+, the luminescence remained and did
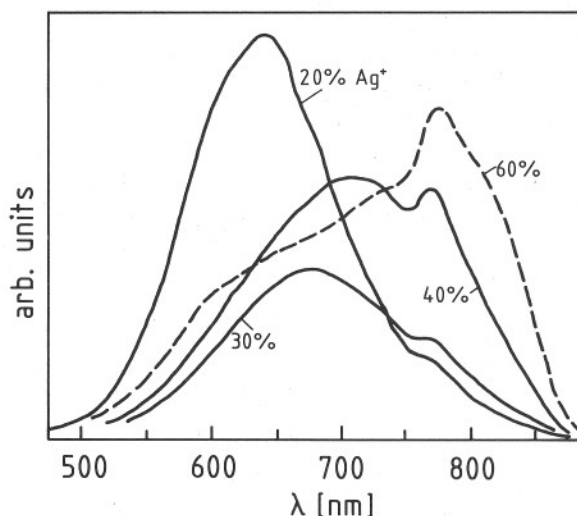

Fig. 4
Spectra of fluorescence at various concentrations of added Ag^+. $2 \cdot 10^{-4}$ M CdS, $2 \cdot 10^{-4}$ M polyphosphate. The Ag^+ concentration is given in percent of the equivalent CdS concentration

not fall down to the small value observed for the $5 \cdot 10^{-4}$ M solution in Fig. 3.

The spectrum of the fluorescence light is shown in Fig. 4. Up to 20% Ag^+, the shape of the fluorescence band is the same as in the absence of Ag^+, although the intensity is increased. At higher concentrations of Ag^+, the spectrum shifts towards longer wavelengths. At low Ag^+ concentrations, the maximum at 600 nm is stronger than that at 760 nm. At high Ag^+ concentrations, the maximum at 760 nm becomes more pronounced. The spectra in Fig. 4 were not corrected for the lower sensitivity of the fluorimeter detector at longer wavelengths.
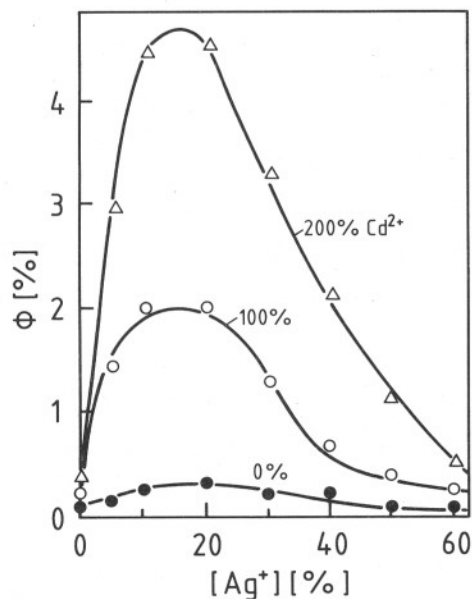
yield in the maximum of the curve was about three times greater than under the best conditions in Fig. 3. Comparing the two figures, one can recognize that the unfavorable effect of high polyphosphate concentrations may be counterbalanced by the favorable effect of high Cd^{2+} concentrations. In Fig. 6, the quantum yield is plotted as a function of the Cd^{2+} concentration. Above about $4 \cdot 10^{-4}$ M, excess Cd^{2+} ions do not further increase the yield. Fig. 6 also shows that Sr^{2+}, Ba^{2+}, and Mg^{2+} ions promote the luminescence even more strongly than Cd^{2+} ions. In^{3+} ions had little effect, and Cs^+ ions did not influence the luminescence. Tl^+ ions acted as quencher.

Fig. 5

Effect of the concentration of excess Cd^{2+} (expressed in percent of the CdS concentration) on the quantum yield of fluorescence. $2 \cdot 10^{-4}$ M CdS; $2 \cdot 10^{-4}$ M polyphosphate; various Ag^+ concentrations

Fig. 7

Spectra (normalized at 300 nm) of a $2 \cdot 10^{-4}$ M CdS sol containing $3 \cdot 10^{-4}$ M $Na_6(PO_3)_6$. pH = 8.
Absorption spectrum: full line; fluorescence excitation spectra: broken lines (immediately after preparation (0), after 20 hours of aging, and additional heating). Wavelength of observation: 650 nm

Fig. 5 shows how excess Cd^{2+} ions, which were added after the preparation of the colloid, influence the fluorescence of a $2 \cdot 10^{-4}$ M CdS solution which contains $2 \cdot 10^{-4}$ M polyphosphate and silver ions. In the absence of excess Cd^{2+}, the solution fluoresces only weakly (Fig. 3). In the presence of $4 \cdot 10^{-4}$ M Cd^{2+}, the quantum
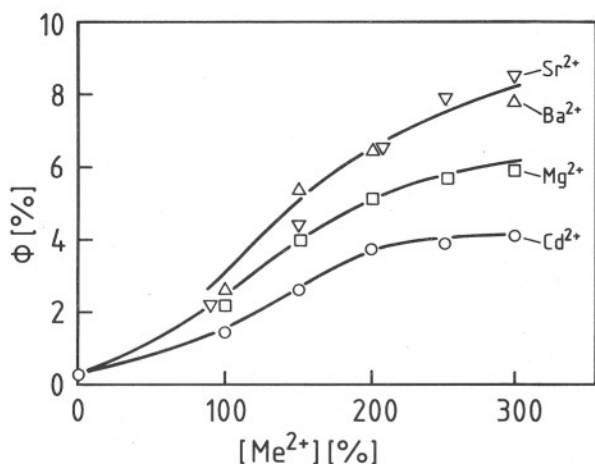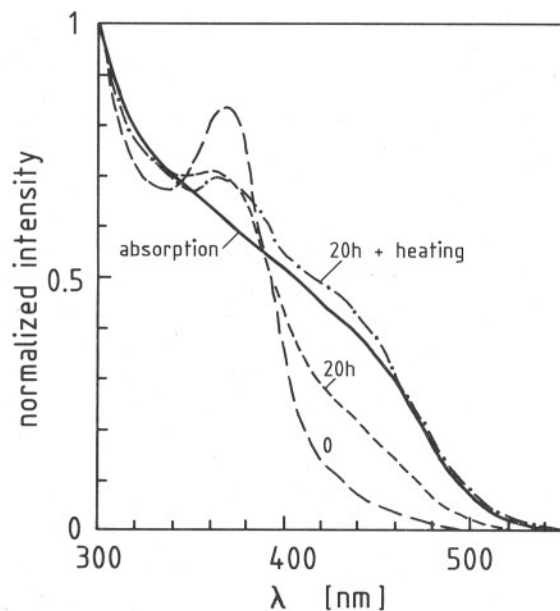
Fig. 6

Quantum yield of fluorescence as a function of the concentration of added metal ions. $2 \cdot 10^{-4}$ M CdS; $2 \cdot 10^{-4}$ M polyphosphate; $6 \cdot 10^{-5}$ M added Ag^+
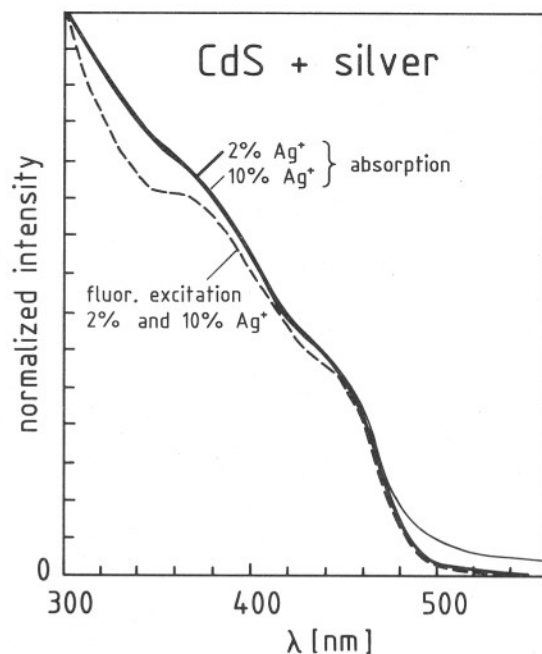
Fig. 8

Absorption and excitation fluorescence spectra of a $2 \cdot 10^{-4}$ M CdS sol containing 2% and 10% Ag^+ ions

In Figs. 7 and 8, fluorescence excitation spectra of different CdS and CdS − Ag$_2$S colloids are shown. It has previously been observed that the fluorescence excitation spectrum generally is not identical to the absorption spectrum of small CdS particles [2]. This effect is demonstrated in Fig. 7, where the absorption spectrum of CdS and its fluorescence excitation spectrum immediately after preparation, after 20 hours of aging, and additional heating (80°C, 30 min) is shown. The four spectra were normalized at 300 nm. The excitation spectrum immediately after preparation has a distinct maximum at 375 nm, and at wavelengths above 400 nm it is much weaker than the absorption spectrum. With increasing time of aging, the excitation spectrum of the sol more and more resembled the absorption spectrum. The latter spectrum did not change upon aging.

Comparing now the spectra of Fig. 7 with those of Fig. 8, where a CdS sol containing 2% and 10% Ag$^+$ ions was investigated, it can be seen that addition of Ag$^+$ ions did not lead to significant changes in the absorption at wavelengths below about 490 nm. However, above 490 nm the absorption was increased and extended to wavelengths longer than that of the threshold of pure CdS. The fluorescence excitation spectrum was practically identical with the absorption spectrum at 2% Ag$^+$. At Ag$^+$ concentrations higher than 2% the fluorescence excitation spectrum did not change anymore, although the long wavelength tail in the absorption spectrum became stronger. It thus seems that 2% Ag$^+$ ions have the same effect on the excitation spectrum as the 20 hours of aging plus heating in Fig. 7.
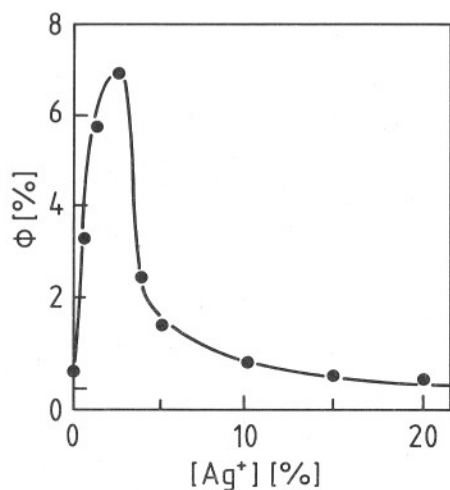
Fig. 9
Quantum yield of fluorescence of co-colloids of CdS and Ag$_2$S of various compositions

CdS − Ag$_2$S Co-Precipitated Sols

Fig. 9 shows the fluorescence quantum yield of colloids which were prepared by simultaneous precipitation of Cd^{2+} and Ag$^+$ ions with NaSH. In principle, a similar dependence of the quantum yield as a function of the silver concentration was obtained as in the experiments of Fig. 3. However, the maximum yield appeared at the much lower silver concentration of 5% and the quantum yields were substantially higher. The pure Ag$_2$S colloid did not fluoresce in the visible. With respect to the changes in the shape of the fluorescence band, similar observations were made as in the experiments of Fig. 4. At Ag$^+$ concentrations smaller than 5% (i.e. the Ag$^+$ concentration where maximum yield was observed), the band had the same shape as in the absence of silver, and at high concentrations it shifted towards longer wavelengths.

Mixtures of CdS and Ag$_2$S Colloids

When a solution of yellow-green CdS ($2 \cdot 10^{-4}$ M CdS; $5 \cdot 10^{-4}$ M polyphosphate), the fluorescence of which was weak, is mixed in

the ratio 9:1 with a solution of Ag$_2$S colloid ($2 \cdot 10^{-4}$ M Ag$_2$S; $3 \cdot 10^{-4}$ M polyphosphate), which did not fluoresce, and 300% Mg^{2+} or Ba^{2+} ions were added, a brightly-red luminescing solution was obtained. Note, that this bright luminescence occured only after the addition of the metal ions. The decay of this luminescence as measured by single photon counting was multi-exponential and extended over several 100 ns.
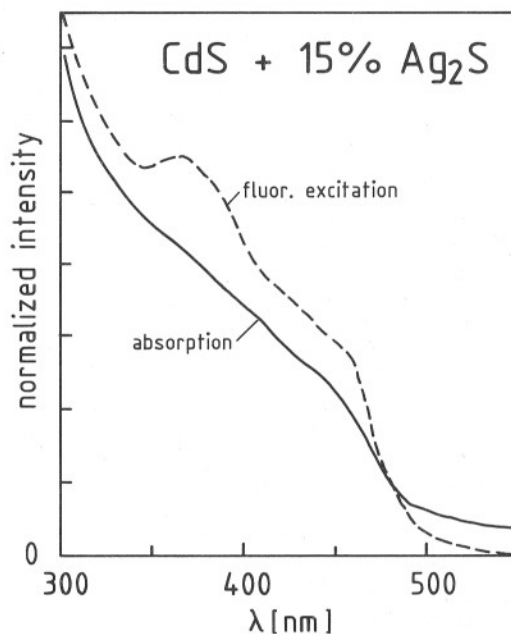
Fig. 10
Fluorescence excitation spectra of a CdS solution and a solution obtained by mixing a CdS and an Ag$_2$S solution and adding 300% Mg^{2+}

Fig. 10 shows the changes in the spectra which occured upon addition of 15% Ag$_2$S sol to the $2 \cdot 10^{-4}$ M CdS sol. Before the addition of colloidal Ag$_2$S, the CdS sol had the absorption and fluorescence excitation spectra shown in Fig. 7. The absorption spectrum after addition of Ag$_2$S (Fig. 10) had the long wavelength tail due to Ag$_2$S. The fluorescence excitation spectrum (Fig. 10) extended to wavelengths longer than the wavelength of the onset of the absorption of pure CdS (compare with Fig. 1), i.e. the added Ag$_2$S exerted the same effect as added Ag$^+$ ions. At shorter wavelengths, the fluorescence excitation spectrum behaves like a mixture of the fluorescence excitation spectra of pure CdS (Fig. 7) and of CdS plus 2% silver (Fig. 8), since the exciton maximum at 345 nm was still present and the fluorescence intensity above 400 nm strongly increased. When Ba^{2+} ions were added to the sol of Fig. 10, the intensity of the luminescence was drastically increased as described above. However, the normalized fluorescence excitation spectrum was practically the same as in Fig. 10 (i.e. before addition of Ba^{2+} ions).

Q-CdS Sols with Particularly Strong Luminescence

In the preceding sections the various factors determining the fluorescence yield were investigated, the highest quantum yields observed lying close to 10%. High Cd^{2+} or other metal concentration, mutual attachment of colloidal particles, and addition of Ag$^+$ ions played an important role. It was found that the fluorescence yield could be further increased by at least a factor of 5 by aging the Q-CdS sol during a few days before the addition of metal ions. Moreover, it was found that the dilution of CdS sols with methanol drastically increased the quantum yield of fluorescence.

A sol with a strong blue luminescence was obtained upon addition of 400% excess Cd^{2+} ions to the Q-CdS sol after thermal aging for one day. Fig. 11 shows the fluorescence spectrum of the sol before and after addition of the excess Cd^{2+} ions (curves 0 and
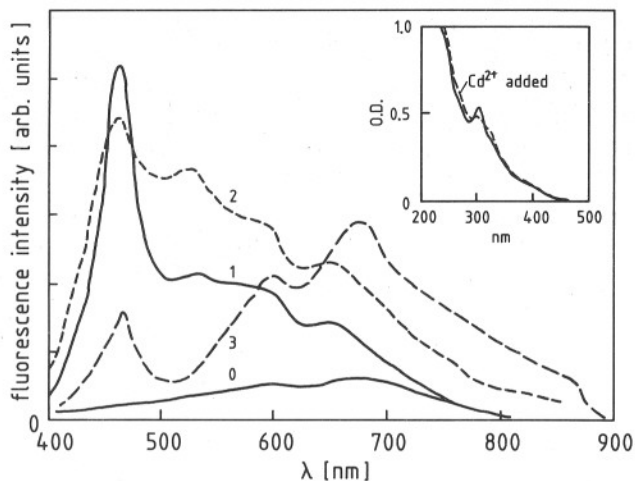
Fig. 11

Fluorescence spectrum of an aged Q-CdS sol (0) and after addition of metal ions (1,2,3). Excitation at 360 nm.
1: 400% Cd^{2+} ions added; 2 and 3: 10% and 30% Ag^+ ions added to solution 1; CdS concentration: $2 \cdot 10^{-4}$ M; polyphosphate concentration: $3 \cdot 10^{-4}$ M; Inset: Absorption spectrum of aged Q-CdS before and after addition of 400% Cd^{2+}

1, respectively). The inset in the figure shows that the absorption spectrum changed little upon addition of the Cd^{2+} ions. The fluorescence band at long wavelengths was increased and a relatively narrow band appeared at 480 nm. The increase at long wavelengths could also be brought about by adding Mg^{2+} or Sr^{2+} ions, while the 480 nm band was not produced by these ions. Curves 2 and 3 in Fig. 11 are the spectra observed after the respective additions of 10 and 30% Ag^+ ions to solution 1. The intensity of the 480 nm band was decreased by Ag^+ ions while that of the long wavelength band was increased. Note that the latter had more than one maximum. The fluorescence color was orange-red for solutions 0 and 3, blue for solution 1, and green for solution 2. Because of the large width of the fluorescence spectrum these colors appeared on an underground of white fluorescence light. Solutions 1, 2 and 3 had a fluorescence quantum yield close to 40%.

A Q-CdS sol fluorescing with a quantum yield of 70% was prepared as follows. In a solution of $1 \cdot 10^{-3}$ M polyphosphate, $4 \cdot 10^{-4}$ M $Cd(ClO_4)_2$ and $4 \cdot 10^{-4}$ M EDTA a pH of 7.8 was established by adding NaOH or triethylamine. $1 \cdot 10^{-4}$ M freshly prepared NaSH (in 0.1 M solution) was added. Subsequently $1 \cdot 10^{-3}$ M $Cd(ClO_4)_2$ was rapidly added (using a 0.1 M solution). The absorption spectrum of the solution contained a pronounced maxima at 300 nm as shown by Fig. 12. The fluorescence spectrum consisted of a broad

band with maximum at 500 nm and the quantum yield was 15%. An increase in the excess Cd^{2+} concentration up to $2 \cdot 10^{-3}$ M and of the pH to 11.5 caused the fluorescence intensity to increase by almost a factor of four. The colorless solution became slightly yellow and the exciton maximum shifted to 320 nm.
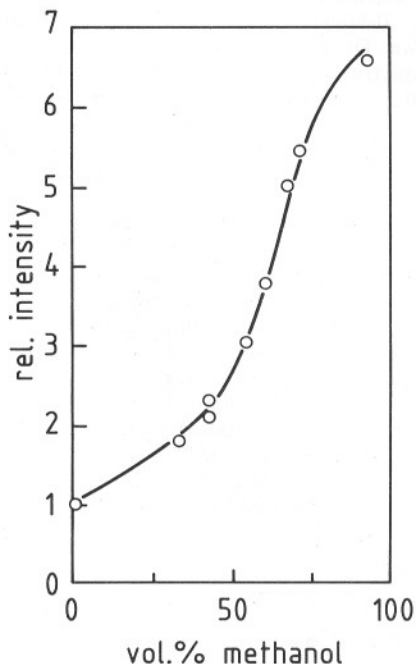
Fig. 13

Fluorescence intensity of Q-CdS as a function of the composition of the water-methanol solvent mixture

In the experiments of Fig. 13, a Q-CdS sol having a concentration of $4 \cdot 10^{-4}$ M was diluted by a factor of 15 by various water-methanol mixtures. The relative fluorescence intensity was plotted as a function of the composition of the solvent mixture. It can be seen that the intensity is greatly increased at high methanol concentrations, the largest intensity corresponding to a quantum yield of almost 100%. That the observed effect was caused by the change in solvent composition and not simply by the dilution was checked by diluting the stock solution to different degrees with 75:25 methanol-water. The quantum yield was independent on the CdS concentration. It was also observed that the fluorescence was slightly shifted to shorter wavelengths with increasing methanol content of the solvent. Between pure water and 95% methanol solvent this shift was 20 nm.

Discussion

The luminescence of macrocrystals of CdS doped with silver has been presented in numerous papers [9, 10]. There is an important difference between the luminescence of colloidal particles and the macrocrystal: In the case of macrocrystalline CdS, doping levels of less than one per mille produce the observed effects, while very much higher silver concentrations are necessary in the colloids. As already mentioned, these concentrations are far above the concentration of 1% up to which Ag_2S can dissolve in the CdS lattice. The effects have, therefore, to be attributed to islands of Ag_2S in or on the CdS particles and the locus of luminescence is believed to be the interphase region between the CdS and Ag_2S parts of the agglomerate.

The main reason for attributing the effects to these islands lies in the observation that all three methods of preparing CdS−Ag_2S solutions lead in principle to the same result.
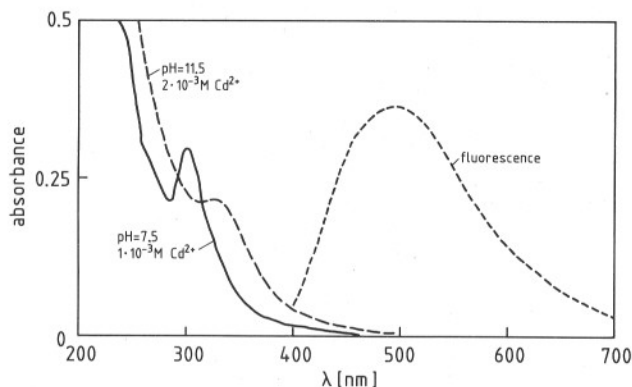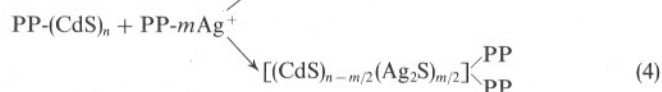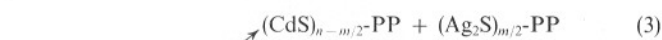

Fig. 12

Absorption and fluorescence spectra of a Q-CdS sol containing $1 \cdot 10^{-4}$ M CdS, $1 \cdot 10^{-3}$ M polyphosphate, $4 \cdot 10^{-4}$ M EDTA and various amounts of excess Cd^{2+} ions

Coprecipitation of Cd^{2+} and Ag^+ ions, subsequent Ag^+ addition to a CdS colloid, and mixing of CdS and Ag_2S colloids had similar effects. Another reason is the enormous influence of the polyphosphate stabilizer, which strongly complexes colloidal CdS particles (Eq. (1)) and makes their surface less accessible to Ag_2S islands.

In the experiments of Fig. 3 it was shown that silver added to CdS solutions promoted the fluorescence the strongest effect occurring at the lowest polyphosphate concentration of $2 \cdot 10^{-5}$ M. Silver ions were also adsorbed by the polyphosphate chains. The effects can be explained by the following scheme:

$$PP\text{-}(CdS)_n + PP\text{-}mAg^+ \nearrow (CdS)_{n-m/2}\text{-}PP + (Ag_2S)_{m/2}\text{-}PP \quad (3)$$
$$\searrow [(CdS)_{n-m/2}(Ag_2S)_{m/2}] \begin{matrix} PP \\ PP \end{matrix} \quad (4)$$

The product of the reaction are either $(Ag_2S)_{m/2}PP$, i.e. an Ag_2S island on a polyphosphate chain (Eq. (3)) or an island on a CdS particle both being complexed to the same chains (Eq. (4)). In the first case, which occurs at high phosphate concentrations, separate CdS and Ag_2S particles are formed and the fluorescence of CdS is not much influenced. In the second case, which we believe to occur at low phosphate concentrations, the intensity of the luminescence is increased. The aggregate formed in the latter case (Eq. (4)) is rather stable and cannot be converted, by subsequent addition of polyphosphate, into the separate aggregates of Eq. (3). In the case of co-precipitation, a greater number of smaller Ag_2S islands possibly grows onto the CdS particles, the result being a larger interphase area. This may explain why the effects occur at lower silver concentrations (Fig. 9).

The promoting effect of added divalent ions (Figs. 5 and 6) can also be understood by the mechanism of Eqs. (3) and (4). As these ions are strongly adsorbed on the polyphosphate chains, less binding sites for CdS or Ag_2S are available. The metal ions therefore produce the effect as a decreased polyphosphate concentration: The Ag_2S islands are in contact with the CdS particles and the luminescence intensity is increased. Perhaps most convincing in this respect are the experiments in which separate solutions of CdS and Ag_2S were mixed and a divalent metal ion was added.

The question about the nature of the luminescence centers at the $CdS-Ag_2S$ interface arises. The orange-red luminescence of CdS in the absence of silver is attributed to the recombination of trapped charge carriers. As excess Cd^{2+} ions increase and excess SH^- ions decrease the intensity of fluorescence [1] it seems most probable that anion vacancies are involved. At low silver concentrations where the Ag_2S islands are small, such anion vacancies are possibly formed in the attachment region between the Ag_2S and CdS phases. At higher silver concentrations where the interphase consists not only of a small spot but of a larger area, new centers, such as double vacancies, may be formed which cause the fluorescence band to move towards longer wavelengths (Fig. 4).

The fluorescence excitation spectra of Figs. 7 and 8 are explained in the following way. A freshly prepared CdS colloid contains particles of different size, the particles of smaller size start to absorb at wavelengths substantially lower than the threshold of 515 nm of the bigger particles. The quantum yield of fluorescence of the smaller particles is much higher than that of the bigger ones. Although the percentage in weight of the smaller particles is not great, the excitation fluorescence spectrum is mainly determined by the smaller particles, i.e. the onset of absorption seems to be shifted to shorter wavelengths and the typical band of the exciton-transition appears at 375 nm (Fig. 7). Upon aging, the bigger particles fluoresce more efficiently and the smaller particles become bigger. This aging process is not accompanied by large changes in the absorption spectrum. However, the fluorescence excitation spectrum approaches the shape of the absorption spectrum (Fig. 7).

The fact that a pronounced excitonic maximum appears in the fluorescence excitation spectrum of the small particles in the CdS sol means that this state can decay into trapped charge carriers which then emit the 650 nm fluorescence upon their recombination. As is further discussed below, the lifetime of the excitonic state for direct radiative recombination is much longer than the time required for the decay into defect states, i.e. the direct fluorescence at wavelengths close to 375 nm does not occur.

At low Ag^+ ion concentration in Fig. 8 where a large part of the added silver can be incorporated into the CdS lattice, the fluorescence excitation spectrum of the freshly prepared colloid is practically identical to the absorption spectrum, and the fluorescence can still be excited by light of wavelengths longer than the threshold wavelength of pure CdS. The added Ag^+ ions have two effects: 1) They have the same effect as aging of the pure CdS, and we explain this as an activation of the bigger CdS particles by incorporated Ag^+, i.e. by an increased fluorescence quantum yield. 2) The extension of the spectral response of the fluorescence excitation to longer wavelengths is attributed to the action of the silver centers which are incorporated into the CdS phase. Light quanta with an energy less than the bandgap energy of CdS are able to excite electrons from these centers into the conduction band or excitonic states of CdS. This conclusion is similar to the one drawn by Reber and Rusek [7] to explain the spectral response of the $CdS-Ag_2S$ photocatalyst in H_2 evolution experiments.

An increase in the concentration of added Ag^+ ions from 2 to 10% did not change the shape of the fluorescence excitation spectrum, although the absorption of the solution was substantially increased at longer wavelengths (Fig. 8). We believe that the fluorescence excitation spectrum is entirely determined by the silver centers in the CdS lattice which cannot exceed 1% [8]. Additional Ag^+ ions in the solution form the Ag_2S phase mentioned above. Light absorption in this phase does not increase the fluorescence intensity of the $CdS-Ag_2S$-complex. However, as discussed above, the fluorescence efficiency of excitation in the CdS phase (containing about 1% incorporated silver) is strongly increased by the attached Ag_2S phase.

Our experiments on the preparation of strongly fluorescing CdS sols show that it is possible to modify the colloids by suitable additives. In the usual colloids, where the quantum yields of fluorescence are just a few percent, the radiationless recombination of the charge carriers is the prevail-

ing process competing with fluorescence. The radiationless recombination is a thermally activated process which generally becomes less efficient at lower temperatures [11, 12]. Whether the recombination occurs with or without radiation depends on the nature of the defect states on the surface of the particles, and it is conceivable that these states can be influenced by adsorbed substances, for example by adsorbed Ag_2S. It should also be kept in mind that a colloid may possess a relatively narrow fluorescence band close to the onset of absorption besides the broad band at longer wavelengths [2]. This narrow band is attributed to direct emission from the excitonic state generated by light absorption. As indicated in Fig. 14, the fluorescence from this state occurs with a lifetime τ_e. On the other hand, the excitonic state may cross over with lifetime τ_c into states in which the two charge carriers are trapped, and the luminescence is emitted upon the recombination of the trapped carriers. This latter process occurs with a relatively long lifetime τ_f. In very small particles, τ_c is often much shorter than τ_e, and the direct fluorescence cannot be seen. Aging may lead to bigger particles where $\tau_c \sim \tau_e$, i.e. both kinds of fluorescence bands are then present [2]. The cross over time τ_c may also be influenced by adsorbed substances which control the number and nature of the traps on the surface.
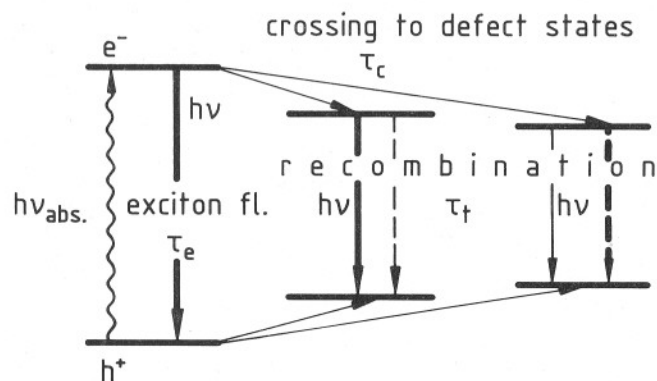

Fig. 14
Term scheme of absorption and fluorescence of small particles ($\rightarrow$: recombination with light emission; $\dashrightarrow$: radiationless recombination)

The increase in fluorescence yield upon substituting the aqueous solvent by methanol (Fig. 13) is another example for the important role which is played by the molecules surrounding the colloidal particles. This observation indicates that water is possibly not a favorable surrounding for luminescing colloidal particles and certain effects of additives could then be discussed in terms of removal of water from the surface of the particles. For example, the promoting effect of a large excess Cd^{2+} concentration and higher pH could be explained as a protective cadmium hydroxide layer being formed around CdS particles.

In Fig. 14, two trap situations for the charge carriers are indicated. One situation where radiationless transition is less important than fluorescence recombination (middle of figure) and another one where recombination without emission of light is predominant (right). The action of methanol could consist of blocking the defect sites on the surface at which the radiationless recombination occurs. This would also explain why the band of the emitted light is slightly blue-shifted. A similar conclusion has been drawn recently by McLendon and coworkers [13] in a fluorescence study on a-particles of Cd_3As_2 [14]. All these observations make one suppose that it may become possible to prepare colloids of different luminescence colors in the liquid and solid state by surface modification procedures.

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