

Photochemistry of Colloidal Semiconductors

32. Reactions and Fluorescence of AgI and AgI–Ag₂S Colloids

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When Ag⁺ ions are precipitated with I⁻ ions in the presence of poly (N-vinyl pyrrolidone) or poly (vinyl alcohol) the AgI colloid forms slowly (during minutes or hours, depending on conditions), the changes in the absorption spectrum indicate the presence of unusual AgI structures during the first stages of particle growth. Size quantization effects are partly responsible for these changes. — AgI colloids with 10% excess of I⁻ do not photolyse under continuous illumination. However, intermediates can be detected in flash photolysis experiments. In the presence of sulfite, silver is formed, the quantum yield lying in the 10⁻⁴ range. Greater yields of silver (10⁻³ to 10⁻²) are observed with solutions containing excess Ag⁺ ions. Less silver is produced in acidic solutions and the silver signal in the flash experiments decays more rapidly. These effects are attributed to the re-oxidation of small silver clusters formed on the colloidal particles by H⁺ ions. — AgI colloids have a weak fluorescence close to the threshold of absorption. It is blue-shifted with decreasing particle size (size quantization effect). The fluorescence is quenched by small amounts of silver deposited on the particles. It is also quenched by an Ag₂S deposit. Under these circumstances a new fluorescence having three maxima in the red and infrared appears. This new fluorescence is red-shifted with increasing size of the silver deposit (size quantization of Ag₂S). The fluorescence is explained in terms of electron transfer from AgI (conduction band) to the hole captured at the AgI–Ag₂S interface. Size quantization effects are also believed to play a role in the sulfur-sensitization of photographic plates.

Introduction

Although silver halides, as the most important component of photographic plates, have been investigated quite thoroughly with respect to their photochemical properties in

gelatine emulsions [1], little is known about light induced reactions in small colloidal particles of these materials in aqueous solution. During the past years a new branch of colloid chemistry has arisen where chemical reactions of the

charge carriers generated upon light absorption in small semiconductor particles are being studied [2]. In the present paper, the preparation of colloidal AgI is reported and its basic photochemical properties, such as corrosion and fluorescence, are described. Furthermore, the fluorescence of AgI—Ag₂S sandwich colloids was investigated and a mechanism proposed in which size quantization of the particles (increase in band gap energy with decreasing particle size) plays an important role.

The AgI colloids were made by precipitating silver ions by iodide in the presence of an organic polymer as stabilizer. Various polymers were used. An interesting effect was observed as the nature of the polymer had an important influence on the kind of colloid formed. This effect is still far away from being explainable, and is just one example of our lack of understanding of the interaction between polymer stabilizers and colloidal particles.

Experimental

The colloids were prepared by rapid addition, under vigorous stirring, a few ml 10^{-2} M KI solution to 100 ml $(1-5) \cdot 10^{-4}$ M AgClO₄ solution containing the stabilizing polymer. Generally, 10% excess iodide was used. In the cases where excess Ag⁺ was to be in the solution, the colloidal solution with 10% I⁻ excess was first prepared and then the desired amount of Ag⁺ added. When H₂S was to be added to an AgI sol, the solution was saturated with argon before the desired amount of H₂S was injected through a septum into the gas atmosphere and the solution vigorously stirred. The polymers were commercial samples of poly(vinyl alcohol), PVA, poly(N-vinyl pyrrolidone), PVP, and poly(ethylene glycol), PEG. They were purified by precipitation, dissolution in water and removal of the solvent by freeze-drying.

Illuminations were performed with a xenon lamp using a 10 cm water filter and a 280 nm cut-off filter. In the cases where the quantum yield was to be determined, monochromatic light was used and Aberchrome 540 applied to determine the photon flux. The flash photolysis experiments were carried out as previously described [3] (using a 6 cm cell and a xenon flash lamp in the two focuses of an elliptical cavity and a 100 W quartz halogen lamp with different interference filters to produce the analyzing light). The dose per flash was $1.6 \cdot 10^{-4}$ M photons absorbed.

Fluorescence measurements were made with an equipment consisting of a 450 W Xe lamp in combination with a CGK McPherrson monochromator as excitation light source, a Spex double monochromator, type 1672, with single photon counting detector for uv-vis emission light, and a Spex monochromator, type 1681, with a nitrogen cooled Ge detector (North-coast) sensitive between 600 and 1600 nm. All signals were digitized, data processing occurring with a PDP 11/23 computer. Emission spectra were corrected for the spectral response of the measuring system.

Results

Absorption Threshold and Particle Size

Figs. 1 and 2 show the absorption and fluorescence spectra of AgI sols stabilized by PVA. The spectra were taken 30 min after preparation of the sols. In the case of Fig. 1, the polymer was present during precipitation, in the case of Fig. 2 it was added immediately afterwards. Both the exciton maximum (411 nm in Fig. 1 and 420 nm in Fig. 2) and the maximum of the fluorescence band (425 nm in Fig. 1 and 433 nm in Fig. 2) are shifted by 13 to 14 nm. Fig. 3 shows the X-ray diffraction diagrams of the two samples (after the solvent had been removed by freeze-drying). The lines are much broader in the case of the sample from Fig. 1, which indicates that it contained smaller particles. Mean particle sizes were calculated using Scherrer's equation [4]: $d = k \cdot l / \beta \cdot \cos \theta$ where β is the half-width of the diffraction peak, l the X-ray wavelength (1.542 Å) and

k a geometric factor taken to be 1. A mean size of 40 Å was obtained for the particles in Fig. 1 and about 200 Å for those in Fig. 2.

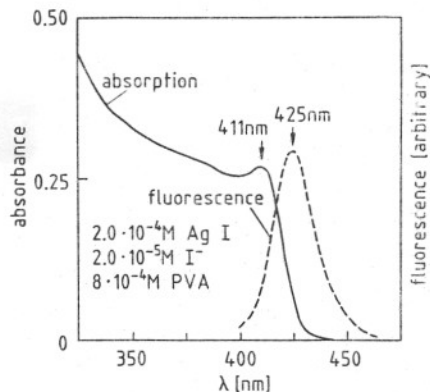


Fig. 1

Absorption and fluorescence spectra of AgI stabilized by PVA. Polymer present during precipitation. Wavelength of fluorescence excitation: 366 nm

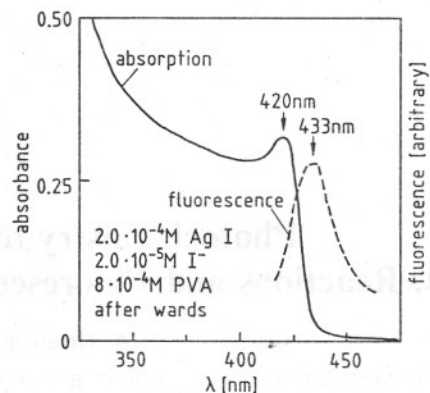


Fig. 2

Absorption and fluorescence spectra of AgI stabilized by PVA. Polymer added after precipitation

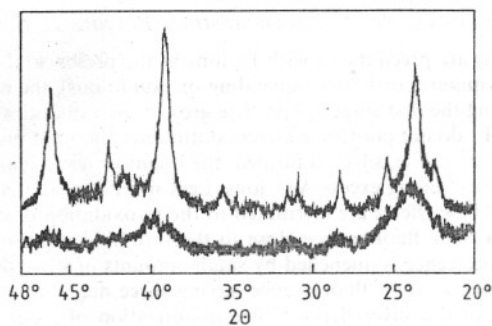


Fig. 3

X-ray diffraction diagrams for the AgI colloids formed in the experiments of Fig. 1 (lower) and Fig. 2 (upper curve)

Temporal Development of the Absorption Spectrum

Neither the absorption nor the fluorescence of the silver iodide sols were fully developed shortly, i.e. minutes, after precipitation. When the colloid was made without a stabilizing polymer, the absorption spectrum showed the exciton peak immediately after preparation. Within a few hours, the peak became sharper, and within days a long wavelengths tail due to scattering by larger particles developed. This can be seen from Fig. 4. It is also recognized that the position of the peak moves towards longer wavelengths with increasing age of the solution.

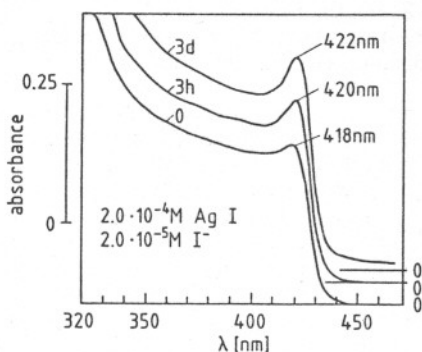


Fig. 4

Absorption spectrum of colloidal AgI at different times after precipitation. No polymer stabilizer present

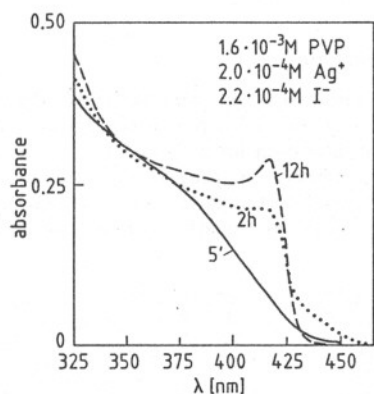


Fig. 5

Temporal development of the absorption spectrum of colloidal AgI in a solution containing PVP

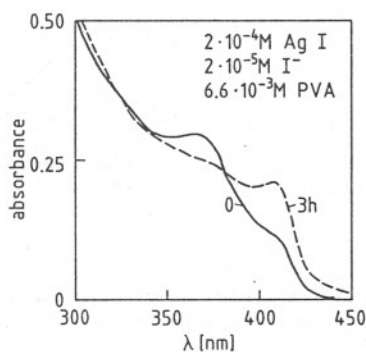


Fig. 6

Temporal development of the absorption spectrum of colloidal AgI in a solution containing PVA

In the presence of PVP and PVA, the absorption spectrum developed more slowly and its shape changed remarkably especially shortly after precipitation. Fig. 5 shows this effect for a PVP containing solution. After 5 min a rather structureless absorption increase toward the uv, with a threshold at about 450 nm, is observed. After 2 h the exciton band is already present. In addition there is a remarkable increase in the 425 to 460 nm range. After 12 h a state is reached where the spectrum no longer changes with time: A rather sharp exciton band had evolved with a steep threshold at 430 nm. The fluorescence is weak in the beginning and becomes stronger during the 12 h ripening. These phenomena indicate that complex rearrangement processes of the AgI precipitated on the polymer matrix take place. The higher the PVP concentration, the longer the duration of the processes.

Fig. 6 shows the results of experiments with a solution containing PVA. Shortly after preparation the absorption spectrum (0) contained a weak peak of the exciton transition at 415 nm and a more pronounced maximum at 360 nm. Upon aging, the latter became weaker and the 415 nm maximum more pronounced. The fluorescence intensity was weak immediately after precipitation and increased upon aging.

When PEG was used as stabilizer, the absorption spectrum reached its final shape after relatively short times. The exciton maximum is well developed and rises steeply below the threshold as can be seen from Fig. 7 (spectrum 0). Solutions containing PEG above $1 \cdot 10^{-3}$ M were clear and did not change for weeks. Solutions of lower polymer concentration became opalescent, indicating that the AgI particles grew noticeably. The fluorescence band was twice as strong as in solutions containing PVA or PVP.

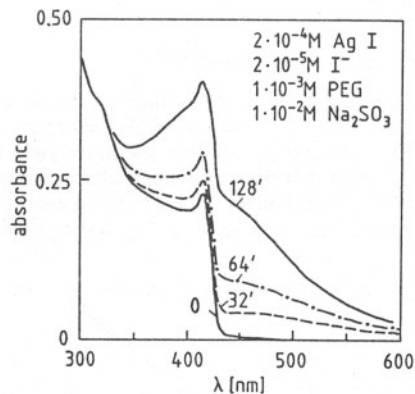


Fig. 7

Illumination of AgI sol stabilized by PEG and containing sodium sulfite. Spectrum at various times of illumination

Photolysis of Colloidal AgI

The silver iodide colloids were not photoactive with respect to the formation of silver or iodine. Illumination for one day with the intense light of a xenon lamp did not produce any changes in the absorption spectrum, regardless whether the solution was illuminated under argon or oxygen. However, substantial changes took place when the de-aerated solution, to which sodium sulfite had been added, was illuminated. As can be seen from Fig. 7, the absorption increased at all wavelengths, the relative increase being particularly strong above 450 nm. The new absorption is ascribed to silver metal deposited on the colloidal AgI particles.

In order to measure the amount of silver formed, its absorption coefficient had to be determined. This was possible in a radiation chemical experiment in which the reduction of AgI was carried out in a controlled manner. When an AgI solution containing 0.1 M methanol was exposed to γ -rays, the same absorption increase as

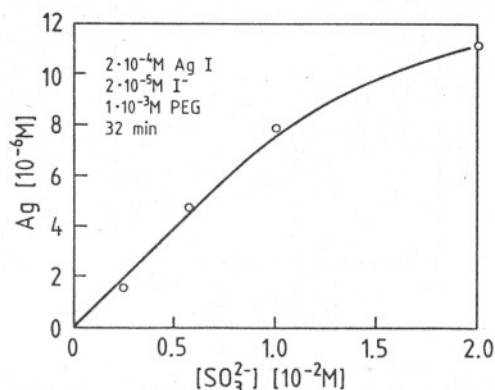


Fig. 8

Concentration of silver formed as a function of sulfite concentration. Illumination time: 16 min

in Fig. 7 was observed. Reducing radicals, such as hydrated electrons and hydroxy methyl radicals, are known to be formed in the radiolysis of aqueous methanol solutions, the total yield of reducing species being 6 radicals per 100 eV absorbed radiation energy [5]. When a radical reacts according to $\text{AgI} + \text{CH}_2\text{OH} \rightarrow \text{Ag} + \text{CH}_2\text{O} + \text{H}^+ + \text{I}^-$, ions are formed and from the increase in conductivity one can show that all radicals generated reacted with the colloidal particles. In other words, the amount of reduced silver is known in this experiment and the absorption coefficient can be determined from the measured absorption increase. At 450 nm, $\epsilon = 8750 \text{ M}^{-1} \text{ cm}^{-1}$ was found.

Fig. 8 shows how the amount of silver depends on the sulfite concentration. At low concentrations, the silver yield is proportional to the sulfite concentration. At higher concentrations, the yield strives toward a limiting value. The quantum yield for silver formation at $[\text{SO}_3^{2-}] = 2 \cdot 10^{-2} \text{ M}$, was found to be $5 \cdot 10^{-4} \text{ Ag atoms/photon absorbed}$.

Fluorescence and Fluorescence Quenching

The fluorescence intensity of the AgI colloids depended rather strongly on the temperature. Fig. 9 shows an Arrhenius plot in the range from 0 to 30°C. As the fluorescence quantum yield is very low (< 0.01) and assuming that the competing radiationless recombinations are temperature dependent with activation energy E (the radiative recombinations of the charge carriers having no activa-

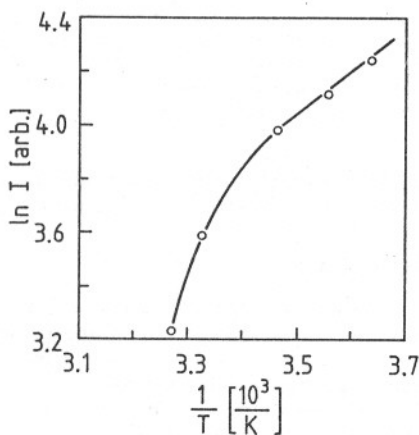


Fig. 9

Arrhenius plot of the fluorescence intensity vs. temperature

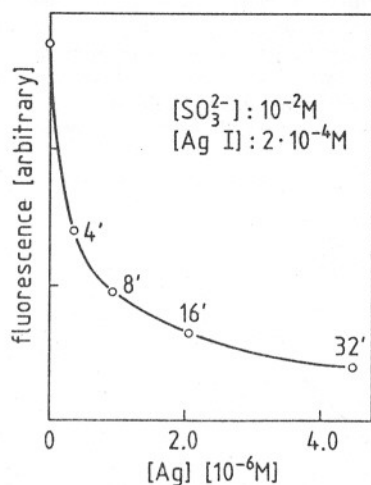


Fig. 10

Illumination of an AgI sol containing sulfite. Fluorescence intensity as a function of the concentration of silver formed. The numbers on the experimental points give the illumination times. Wavelength of excitation: 366 nm

tion energy), the fluorescence intensity should be proportional to $\exp(E/RT)$. The bent line obtained in Fig. 9 indicates that processes with different activation energies contribute to the radiationless recombination.

Addition of $2 \cdot 10^{-4} \text{ M}$ methyl viologen, MV^{2+} , 1,1'-dimethyl-4,4'-bispyridyl dichloride, to an AgI sol did not influence the fluorescence intensity. In the case of other colloidal semiconductors, such as CdS [6, 7] and TiO_2 [8], methyl viologen captures electrons, the result being a decreased fluorescence intensity and often the formation of the blue-colored radical cation MV^+ . Addition of 10^{-2} M sodium sulfite also did not result in the quenching of the fluorescence. However, when this solution was illuminated with a xenon lamp, i.e. when silver was formed (see Fig. 7), the fluorescence intensity rapidly decreased as can be seen from Fig. 10. In this figure, the concentration of silver formed is plotted on the abscissa. 50% quenching is reached at a silver concentration of $4 \cdot 10^{-7} \text{ M}$. The concentration of the silver iodide particles was of the order of 10^{-8} M . Thus roughly some 10 Ag atoms per particle are sufficient to cause significant quenching of the fluorescence.

Excess Silver Reduction

Silver iodide sols with excess Ag^+ were less stable than sols containing an excess of I^- . In fact, PEG practically did not protect the colloid from precipitation even for a short time. The experiments of Figs. 11–13 were carried out using PVA as stabilizer. Fig. 11 shows absorption spectra at various times of illumination. The increase in absorption at all wavelengths indicates the formation of

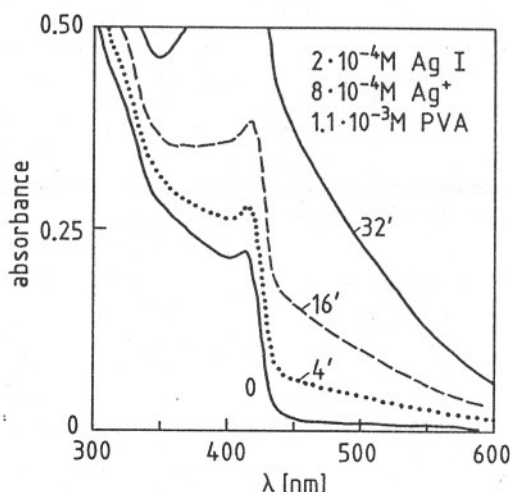


Fig. 11

Illumination of an AgI sol containing excess Ag^+ ions. Absorption spectrum at different illumination times

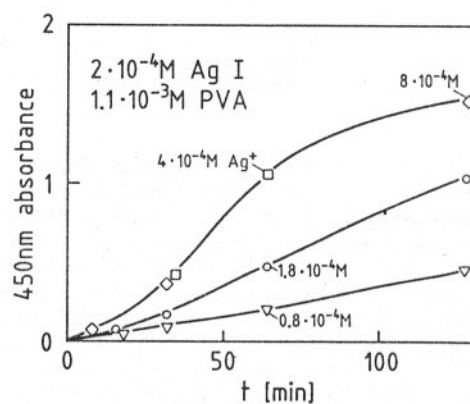


Fig. 12

450 nm absorption of silver formed as a function of illumination time for solutions containing various excess Ag^+ concentrations

silver. Fig. 12 shows the 450 nm absorption of silver as a function of illumination time for solutions containing various concentrations of excess Ag^+ . The silver yield increases with increasing Ag^+ concentration. Above $8 \cdot 10^{-4} \text{ M Ag}^+$, the solutions were no longer stable. In Fig. 13, the silver absorption is plotted vs. time for solutions of different hydrogen ion concentrations (made by the addition of HClO_4). With increasing H^+ concentration, less silver is produced.

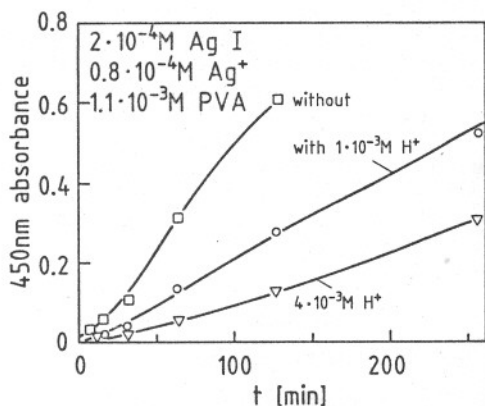


Fig. 13

450 nm absorption of silver formed as a function of illumination time for solutions containing various concentrations of hydrogen ions

The quantum yield of silver formation in a solution of natural pH ($2 \cdot 10^{-4} \text{ M AgI}$, $4 \cdot 10^{-4} \text{ M excess AgClO}_4$, $1 \cdot 10^{-3} \text{ M PVA}$) was $4 \cdot 10^{-3}$ atoms/photon absorbed.

Flash Photolysis Experiments

Immediately after the photo-flash an absorption signal was present at all wavelengths in the 300–700 nm range investigated. In solutions containing excess Ag^+ ions the signal was larger with increasing silver ion concentration until it strived toward a limiting value. This can be seen from Fig. 14. The signal is attributed to the formation of silver during the flash. At the light intensity used, a large number of photons was absorbed in a colloidal particle during

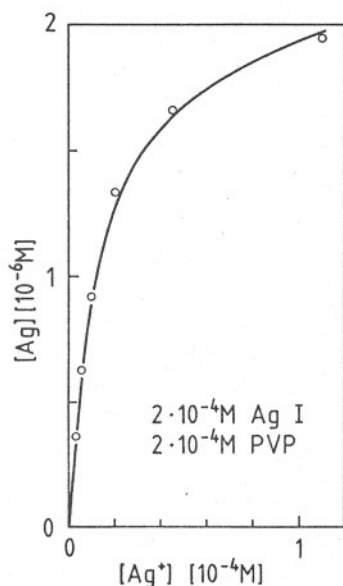


Fig. 14

Flash photolysis of AgI sols containing different amounts of excess Ag^+ . Concentration of silver formed after the flash as a function of Ag^+ concentration

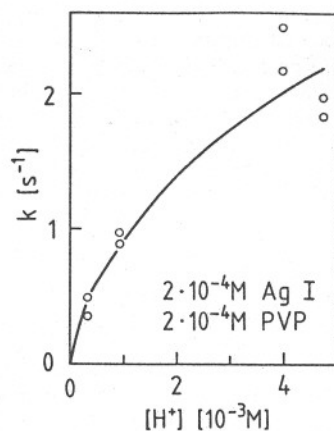


Fig. 15

First order rate constant of the decay of the silver absorption after the flash as a function of the H^+ concentration of the solution

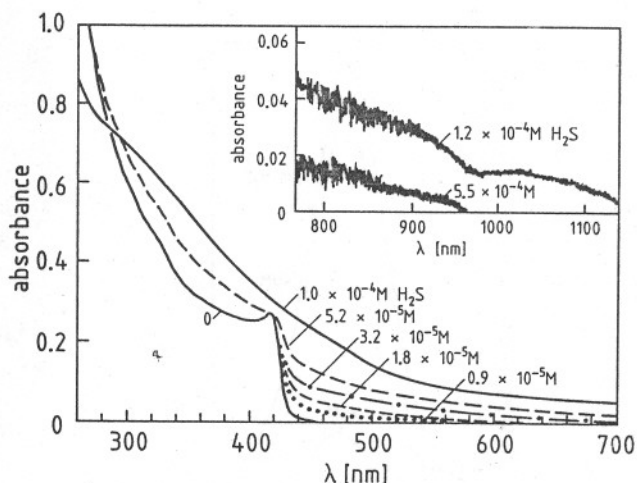


Fig. 16

Absorption spectrum of an AgI sol after addition of various amounts of H_2S . $2 \cdot 10^{-4} \text{ M AgI}$; $2 \cdot 10^{-2} \text{ M PVP}$; $4.0 \cdot 10^{-5} \text{ M I}^-$. Inset: Typical absorption curves in the infrared (from 950 to 1000 nm disturbance by solvent absorption)

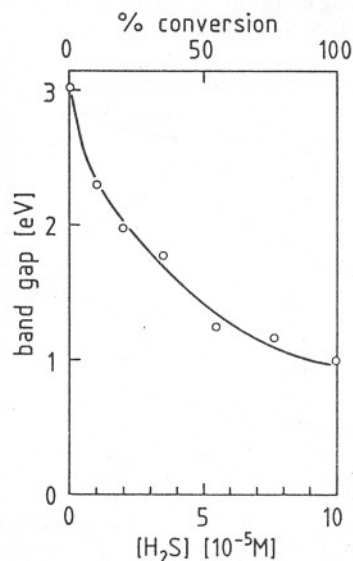


Fig. 17

Band gap of the silver sulfide deposit as a function of added H_2S concentration. Solution as in Fig. 16 (upper abscissa scale: % conversion of AgI to Ag_2S)

the flash. The signal decayed after the flash within several seconds. In acidic solutions, the signal decayed much faster. Fig. 15 shows the first order rate constant as a function of H^+ concentration. At low H^+ concentrations, the rate constant is proportional to $[H^+]$, at higher concentrations it increases more slowly. In solutions containing sodium sulfite (10^{-6} to 10^{-3} M), the signal was as high as in the absence of sulfite, but it did not decay after the pulse.

Sandwich Colloids of AgI and Ag_2S

Fig. 16 shows the absorption spectrum of a $2 \cdot 10^{-4}$ M AgI sol after the addition of various concentrations of Ag_2S . Because of the lower solubility of silver sulfide, H_2S reacts with the colloidal particles to form an Ag_2S deposit. With increasing H_2S addition, the tail toward longer wavelengths becomes more and more pronounced. The wavelength of absorption threshold was determined and the corresponding band gap energy of the Ag_2S deposit calculated. Fig. 17 shows the band gap energy as a function of the concentration of H_2S added (or the % conversion of AgI to Ag_2S). It can be seen that this energy gradually decreases with increasing

conversion until it reaches the value of pure silver sulfide, i.e. approximately 1 eV.

The fluorescence of AgI is quenched by the addition of hydrogen sulfide as is illustrated by Fig. 18a. However, a new fluorescence appears at wavelengths in the red and infrared part of the light spectrum, which is shown by Fig. 18b. The intensity of this fluorescence first increases with increasing H_2S concentration and the maximum is located at 850 nm (1.45 eV photon energy). At higher H_2S concentrations, a second maximum at 1050 nm (1.18 eV) appears which becomes more and more pronounced and shifts toward longer wavelengths. At the highest H_2S concentrations, a third maximum at about 1250 nm (0.99 eV) becomes stronger and stronger and finally is the only maximum present after almost 100% conversion of AgI to Ag_2S . The intensity of the emission strongly decreased at high conversions. The excitation spectrum resembled the absorption spectrum of the AgI- Ag_2S colloid which is an indication that the excitation of both the AgI and the Ag_2S part of the sandwich colloid lead to the infrared fluorescence.

Discussion

Effects of Polymer-Colloid Interaction

A striking effect of certain polymers, such as PVP and PVA, on the kinetics of formation of colloidal AgI was observed in the present studies. The fact that the typical absorption spectrum of AgI (Fig. 4; absence of polymer) did not appear immediately after precipitation but developed during minutes or hours (depending on polymer concentration) shows that certain forms of AgI are present initially which have optical properties quite different from those of the usual AgI forms stable at room temperature.

One of these properties is the shift of the band gap energy in very small particles [2,9]. In the case of AgI, this shift has recently been observed in a pulse radiolysis experiment in which I^- ions were suddenly produced in an Ag^+ ion containing solution and the absorption spectrum measured after different times of particle growth [14]. In the present investigation, the shift of the exciton peak as well as that of the fluorescence band was observed. This is illustrated by Figs. 1 and 2 where the mean particles sizes were 40 and 200 Å, respectively. It might well be that the first AgI agglomerates formed in the precipitation are much smaller and therefore more strongly quantized than the particles in Fig. 1. They are stabilized on the polymer and grow relatively slowly. A broad size distribution of these primary AgI clusters would lead to a smeared absorption, which could explain the rather flat and structureless increase in absorption below the threshold wavelength (Fig. 5, after 5 min). At the present time, one can, however, not rule out that the observed effects are not only due to size quantization but also to the formation of particles with an unusual lattice structure, for example to AgI chains along the polymer matrix. The fact that the exciton peak sometimes has a long tail toward longer wavelengths (even beyond the position of the threshold in macrocrystalline AgI; see Fig. 5, 2 h or Fig. 6, 3 h) could be an indication for the presence of such unusual lattice structures. For example, α -AgI, which normally is stable only at higher temperatures and is of deeper yellow color than the more usual β and γ forms of AgI, could be present in an intermediate stage of particle growth. Slight changes in the position of the excitation peak in AgI particles of rather large size (150–300 Å) have previously been attributed to the conversion from cubic to hexagonal

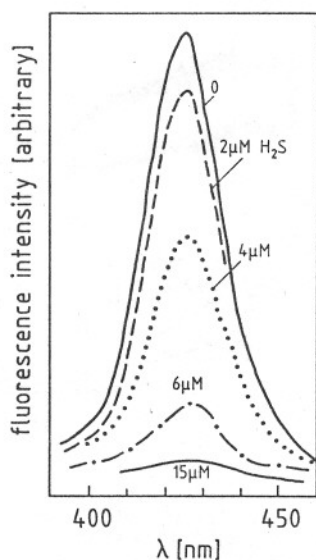


Fig. 18a

Fluorescence quenching of AgI by the addition of various amounts of H_2S . Solution as in Fig. 16

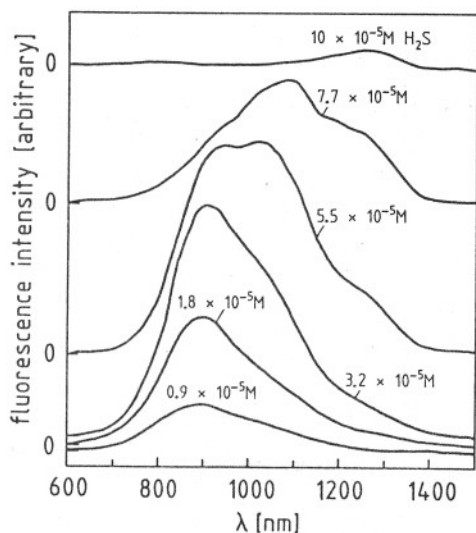


Fig. 18b

Fluorescence spectrum of an AgI sol at long wavelengths after addition of various amounts of H_2S . Solution as in Fig. 16

AgI [10]. The question of the occurrence of unusual lattice structures cannot be answered unambiguously unless one succeeds in stopping the particle growth at an early stage and measuring the X-ray diffraction pattern. Our present results are certainly in a premature state, but, nevertheless, seem to be important in showing that interesting interactions between polymer matrices and inorganic colloids exist and ought to be investigated.

Photochemical Reactions

Electrons in the conduction band and positive holes in the valence band are generated upon light absorption in semiconductor colloids. The fact that intense illumination of AgI sols (containing 10% excess iodide) did not lead to any chemical change could be interpreted as a very efficient recombination of the charge carriers before they initiate reactions. On the other hand, the flash photolysis experiments showed that an intermediate was present immediately after the flash and decayed rather slowly in times > 1 s. This intermediate is thought to be silver metal deposited on the AgI particles and absorbing at all wavelengths in the visible part of the light spectrum. The quantum yield of silver formation, however, is only about 10^{-3} atoms/photon absorbed. It thus seems that the vast majority of the charge carriers indeed recombine rapidly and that only a few form silver and iodine atoms. These atoms finally recombine after a life time of a few seconds the overall yield of photolysis being zero.

In the presence of a reactant for either electrons and holes or silver and iodine atoms, permanent chemical changes occur upon illumination. Silver is formed in the presence of sulfite (Figs. 7 and 8). As sulfite anions probably are not adsorbed on the colloidal particles (which are negatively charged in solutions containing excess iodide) and therefore cannot compete with the recombination of the charge carriers, it is proposed that SO_3^{2-} ions react with the iodine atoms formed. The remaining silver atoms combine with each other and form a deposit on the colloidal particles.

Silver is also formed when the sol is illuminated in the presence of excess Ag^+ ions (Figs. 11, 12 and 14), the yield being about 10^{-3} atoms/photon absorbed at the highest Ag^+ concentration of $8 \cdot 10^{-4}$ M Ag^+ applied. In acidic solutions lower silver yield were observed (Fig. 13) and in the flash experiments the signal present immediately after the flash decayed more rapidly (Fig. 15). The silver atoms formed on the colloidal particles have a high negative redox potential as long as they are isolated or form small clusters [2, 11–15] and in this state can be re-oxidized by H^+ ions. Unfortunately, the complete reaction mechanism for illuminated solutions containing excess Ag^+ ions cannot be given as it is not yet known which oxidation process accompanies the reduction of silver ions. The oxidation cannot consist of the formation of iodide to iodine as the efficient back reaction $2\text{Ag} + \text{I}_2 \rightarrow 2\text{AgI}$ would lead to zero overall conversion. One must therefore assume that either the organic polymer or the aqueous solvent is oxidized. Because of the small conversion rates in these experiments the products of oxidation could not yet be identified.

Only a very small fraction of the recombining charge carriers produces fluorescence light, most of the recombinations

occurring in a radiationless manner. The silver deposit formed during illumination in the presence of sulfite or excess Ag^+ ions acts as a quencher of the fluorescence (Fig. 10). It is concluded that the silver deposit is able to scavenge charge carriers. However, this scavenging process does not result in an increased yield of permanent chemical conversion. It thus seems that the silver deposit simply acts as a mediator for the recombination of charge carriers.

Fluorescence of AgI–Ag₂S Sandwich Colloids

Upon addition of H_2S to an AgI sol, Ag_2S is formed. In the absorption spectrum (Fig. 16) a long wavelengths tail appears. That the silver sulfide formed is attached to the silver iodide particles can be concluded from the fact that the fluorescence of the latter is quenched (Fig. 18a) and that a new fluorescence appears in the infrared (Fig. 18b). The latter effect has already been observed in the case of AgBr particles in photographic plates after sulfur-sensitization. This sensitization is brought about by keeping the emulsion at 55°C for 8 h in the presence of $\text{Na}_2\text{S}_2\text{O}_3$ or $\text{N}_2\text{H}_4\text{CSO}_2$ [16] or by dipping the photosensitive layer for 1 min in a 10^{-4} M Na_2S solution [17]. The AgBr particles acquire an Ag_2S deposit in this way and show the red and infrared fluorescence described above. Similar phenomena have more recently been observed for CdS– Ag_2S sandwiches: When Ag^+ is added to an CdS sol, or when Cd^{2+} and Ag^+ are simultaneously precipitated by H_2S , or when CdS and Ag_2S sols prepared separately are mixed, a strong red fluorescence appears which moves toward longer wavelengths with increasing size of the Ag_2S part and finally disappears. These effects have been explained in terms of recombination of charge carriers at the CdS– Ag_2S interface [18]. Certainly, a common mechanism must be operative in these various systems.

As the silver sulfide deposit on the AgI particles grows with increasing concentration of added H_2S , the onset of absorption moves to longer wavelengths (Fig. 16) and in the fluorescence spectrum the longer wavelengths become more pronounced (Fig. 18b). Chibisov and coworkers [19] have already observed that Ag_2S particles, produced by dosed addition of silver nitrate to a gelatine solution of sodium sulfide, fluoresce at longer wavelengths with increasing particle size in the 30 to 100 Å range, and that the fluorescence intensity becomes lower for the larger sizes. Their explanation was based on the "amorphism" of $(\text{Ag}_2\text{S})_n$ centers of less than 150 Å, only larger particles forming a crystal lattice. In the light of our more recent thinking we interpret both our results, i.e. the red-shift of the absorption threshold in Fig. 16, and the results of the Russian authors as size quantization of the very small silver sulfide particles. They have a band gap much greater than ordinary silver sulfide (Fig. 17).

The term schemes in Fig. 19 enable one to understand how the three maxima in the infrared fluorescence spectrum arise (Fig. 18b). Part a of the figure shows the case where the Ag_2S deposit is very small, the conduction band of Ag_2S lying at higher electronic energy than that of AgI. Illumination into the AgI part of the sandwich colloid leads to the formation of an electron-hole pair. We postulate, in agreement with Chibisov and coworkers on their work with

sulfur sensitized AgBr grains [20], that the hole moves into the valence band of Ag_2S at the interface between the two semiconductor parts. Recombination of the electron in the conduction band of AgI with the hole in Ag_2S produces the fluorescence maximum around 850 nm (1.45 eV). With increasing size of the silver sulfide deposit, the conduction band of Ag_2S moves to lower energies. As long as it is not below the conduction band of AgI, the fluorescence is still produced via the steps in part *a* of Fig. 19. However, when the silver deposit is large enough to have a conduction band at energies below that of AgI, fluorescence can be produced as illustrated by part *b* in the figure: Both the hole and the electron move into Ag_2S , and their recombination leads to the emission around 1050 nm (1.18 eV). Part *c* in Fig. 19 describes the case of a very large silver sulfide deposit which is practically not quantized; in this case the light absorption occurs mainly in the Ag_2S part. The recombination of the charge carriers takes place in Ag_2S and produces the fluorescence around 1250 nm (0.99 eV). Under our experimental conditions one is always dealing with silver deposits

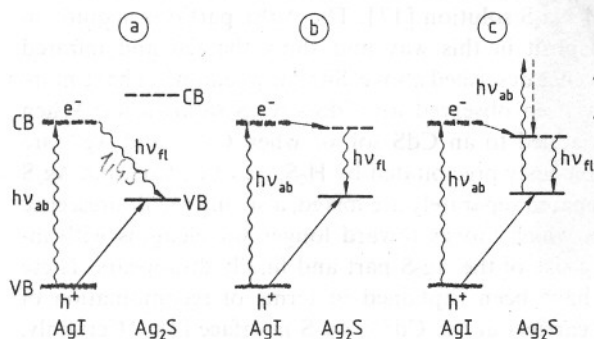


Fig. 19

Term scheme in AgI- Ag_2S colloids. *a*: Small, quantized Ag_2S part. *b*: Larger Ag_2S part. *a* and *b*: Excitation mainly in the AgI part. *c*: Large Ag_2S particles, not quantized, excitation mainly in Ag_2S . Excitation wavelength: 366 nm

of a certain size distribution, all three mechanisms of recombination fluorescence being possible. By varying the amount of Ag_2S , the relative contributions of the three mechanisms change.

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