J. Am. Chem. Soc. 1987, 109, 5649-5655

CV curves only show one peak. Although the spectral data do not prove a two-step charge-transfer mechanism in these pH regions for the smooth Ag electrode, the fact that the SERS and CV curves establish the existence of the intermediate strongly suggests that a two-step mechanism involving overlapped reduction potentials takes place on both types of electrode surface over the entire pH 2–7 region.

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Photochemistry of Colloidal Semiconductors. 20. Surface Modification and Stability of Strong Luminescing CdS Particles

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Abstract: The preparation of CdS sols with a mean diameter between 40 and 60 Å and a relatively narrow size distribution is described. The colloids could be separated as solids, which in turn could be redissolved to give solutions of some 10^{-2} M. Activation of the particles by a cadmium hydroxide precipitate yielded fluorescing samples with a quantum yield exceeding 50%. The blue or green fluorescence occurred close to the band gap energy, which depended on the size of the particles. Violet fluorescing samples of activated ZnS–CdS co-colloids were also prepared. Photoanodic corrosion measurements showed that the activated CdS colloid was 2000 times more stable than the nonactivated one. Under laser illumination the particles became a little larger which is ascribed to an acceleration of Ostwald ripening due to local heating. Extremely intense laser light decomposed the particles into Cd + S.

In the first papers of this series it was shown that colloidal cadmium sulfide in aqueous solution fluoresces and that this fluorescence is efficiently quenched by certain solutes.[1,2] A large number of reports on the fluorescence of colloidal CdS have appeared in the meantime, including both continuous illumination and laser-flash studies.[3-6] The fluorescence is produced upon the recombination of the charge carriers which are generated by light absorption. In most of these studies, no systematic preparative investigations were made to obtain samples having a high quantum yield of fluorescence. In fact, the quantum yield generally was even below 1%, the reason being that the colloidal particles prepared had a lot of defect sites where radiationless recombination of the charge carriers occurred. The environment also affects the fluorescence. For example, CdS in a dry Nafion film luminesces more strongly than in a wet one.[5a]

If the defect sites are located at the surface of the colloidal particles, there appears to be a chance to influence these sites chemically. In fact, it was recently reported in two studies that the fluorescence intensity may be drastically increased by certain surface modification procedures such as exchanging the aqueous solvent by alcohol,[7,8] covering the surface with cadmium hydroxide or silver sulfide,[8] and adsorbing triethylamine.[7] These procedures may also lead to changes in the shape of the fluorescence spectrum, i.e., to changes in the color of the emitted light. The reader may be reminded that the fluorescence color can also be varied by using sols of different particle sizes[9-12] provided that one is operating in the range of extremely small particles where quantization effects due to the spacial confinement of the charge carriers occur.[13,14] These various procedures offer a great variety of possibilities to prepare and investigate luminescing CdS samples having different properties. In fact, one may even ask the question whether inorganic colloids could be substituted for organic dyes in certain electrooptical devices.

In the present paper, detailed descriptions are given for the preparation of strongly luminescing sols of Q-CdS (Q indicates particles showing size quantization effects) and of co-colloids of CdS and ZnS. These samples have fluorescence quantum yields greater than 50%, and another outstanding feature is the relatively narrow width of the fluorescence band. The stability of these colloids was tested in photoanodic dissolution experiments with continuous illumination and high laser intensity irradiation. Fluorescence lifetime and quenching experiments were also carried out.

Experimental Section

Preparation of CdS Colloids. The strong luminescing colloids were prepared in two steps. First, a base sol was made by precipitating Cd^{2+} ions with the stoichiometric amount of injected H_2S. Secondly, the sol was activated by adding first NaOH and then excess Cd^{2+} ions. The base sol had a weak broad fluorescence band between 500 and 700 nm. The activated sol had a very strong fluorescence band close to the onset of absorption. This band was 10 to 100 times stronger than that at the

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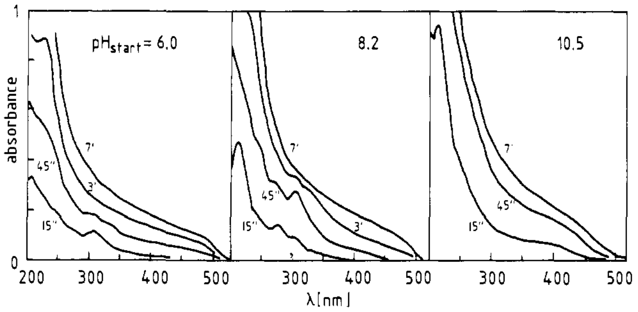

Figure 1. Absorption spectrum at different times after CdS precipitation and at three different starting pH's: 2×10^{-4} M $Cd(ClO_4)_2$; 2×10^{-4} M $(NaPO_3)_6$, 2×10^{-4} M H_2S.

longer wavelengths. A narrow band, however, was obtained only when certain precautions were taken. It is important that the pH of the solution before the precipitation with H_2S is only slightly alkaline and slightly acidic afterwards. The pH before precipitation which we call the "starting pH" determines the color of the fluorescence light after activation of the base sol.

The base sol was made in most of the experiments as follows: a 500-mL solution containing 2×10^{-4} M $Cd(ClO_4)_2$ and 2×10^{-4} M $(NaPO_3)_6$ (Riedel de Haen) was bubbled in a 1-L flask with argon for 15 min. It should be mentioned that the commercial sodium hexametaphosphate consists of polyphosphates with chain lengths up to 450 (PO_3) units. Concentrations given in this paper refer to the formula $(NaPO_3)_6$. The pH of the solution was adjusted to 8.0–8.3 with NaOH. The calculated amount of H_2S was injected into the gas phase and the solution vigorously shaken. It took about 2 min before the solution became yellow. In the experiments of Figure 4, where the influence of the starting pH was to be studied, 200 mL of solution containing 2×10^{-4} M $Cd(ClO_4)_2$ plus 2×10^{-4} M $(NaPO_3)_6$ were used. The flask was equipped with a pH electrode to follow the pH changes during precipitation and with a septum to inject a 1 M $Na_2B_4O_7$ solution to adjust the pH between 7 and 8. In these experiments, borate solution was also added dropwise after the addition of H_2S to keep the pH close to 5 during the development of the CdS particles.

The activation of the base sol consisted of the dropwise addition of 1 M NaOH to establish a pH of 10.5 followed by the dropwise addition of a 1 M $Cd(ClO_4)_2$ solution. The fluorescence intensity was checked from time to time and the addition of Cd^{2+} ions stopped after the fluorescence intensity no longer increased. At this point the solution contained about 6×10^{-4} M excess Cd^{2+} ions.

Apparatus. Absorption spectra were recorded on an Omega 10 spectrophotometer from Bruins Instruments. The scan time was 12 ms. Continuous illuminations were carried out with a 600-W Hg-Xe lamp (Hannovia) in combination with a 10-cm water filter and a WG 360 cutoff filter. Fluorescence spectra were measured with a Shimadzu RF 540 fluorimeter. Fluorescence quantum yields were determined by comparison with fluoresceine or coumarine-2 in methanol, which are known to fluoresce with quantum yields of 1 and 0.9, respectively.

The picosecond studies were carried out with a frequency tripled Nd-YAG laser (JK System 2000 AMS, 355 nm, ca. 8 mJ pulse energy, 100 ps pulse duration). Fluorescence spectra were taken point by point with a monochromator (spectral resolution 10 nm), a fast biplanar photodiode, and a Tektronix R7912 AD Transient Digitizer (time resolution 600 ps). The spectra were corrected for the varying sensitivity of the photodiode at different wavelengths. Lifetimes down to 50 ps could be measured on a Hamamatsu C979 streak camera system. Details of the fast kinetic measurements were recently described.[15] Nanosecond fluorescence lifetimes were measured with a single photon counting apparatus (199 fluorescence spectrometer from Edinburgh Instruments, Ltd).

Particle sizes were determined by transmission electron microscopy. To prepare the samples a drop of the colloidal suspension was applied for 30 s to a copper mesh covered with a carbon film and subsequently removed with a paper tip. Adhesion of the particles was promoted by exposing the carbon film to a glow discharge prior to this procedure.

Results

Effect of Starting pH on the Properties of the Colloid. The absorption spectrum of the solution was recorded at various times after the precipitation. This is shown by Figure 1 for three values of the starting pH. After 7 min the spectrum was always fully developed, the onset of absorption lying close to 500 nm. However, the spectra at shorter times looked quite different for the various values of pH_{start}. For example, the onset of absorption after 15 s was below 400 nm in the cases of the two lower pH_{start} values while it was positioned at a substantially longer wavelength at $pH_{start} = 10.5$. Further, the spectra at the low pH_{start} values had several maxima. Such maxima in the absorption spectrum of extremely small particles which show size quantization effects have already been reported previously.[9,16] The maxima persisted for the longest time in the developing spectrum in the case of pH_{start} 8.2. The electron microscopic inspection revealed that the colloid formed at $pH_{start} = 8.2$ had the most narrow size distribution. It seems that by recording the temporal development of the absorption spectrum one can obtain a rough idea about the final dispersity of the colloid formed.

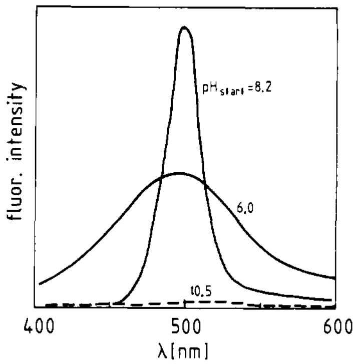

Figure 2. Fluorescence band of the colloids in Figure 1 after activation by adding 2×10^{-3} M NaOH and 6×10^{-4} M $Cd(ClO_4)_2$.

The colloids prepared in the experiments of Figure 1 were now activated by adding NaOH and excess Cd^{2+} ions as described above. Figure 2 shows the fluorescence spectra of the activated sols. Before activation, the sols had a weak fluorescence band in the 500 to 700 nm range. It was a little increased upon activation. However, the main effect of activation consisted of the production of a strong fluorescence band close to the onset of absorption. This band is rather narrow in the sample with $pH_{start} = 8.2$, very broad in the sample of $pH_{start} = 6.0$, and missing in the sample with $pH_{start} = 10.5$.

It became evident from these experiments that colloids with a relatively narrow size distribution and a narrow and intense fluorescence band after activation could be prepared only in a relatively narrow range of pH_{start}. This range which extends between 6.5 and 10.0 was investigated in more detail. First of all, it was found that the average size of the particles increased in this range with decreasing pH_{start} as can be seen from the histograms in Figure 3. Note that this is the size range where the particle size becomes smaller than the size of an exciton in macrocrystalline CdS (60 Å), i.e., where size quantization effects become noticeable. This can be recognized by looking at the absorption spectra a, b, c and the fluorescence spectra a′, b′, c′ of the three activated samples in Figure 4. For the smallest particles, i.e., sample a, the onset of absorption is already shifted to a wavelength clearly shorter than 500 nm. The color of the fluorescence light changed noticeably as indicated in Figure 4. The maximum of the fluorescence band was always positioned at the wavelength of the inflection point in the absorption spectrum which could readily be determined by recording the first derivative of the absorption spectrum. The color of all colloids was yellow. However, at daylight they had a green tinge due to their strong luminescence. The quantum yield was greater than 50% in all three cases.

It was not possible to prepare CdS samples with a strong violet luminescence by using still higher pH_{start} values than in Figure 4. The result was always a colloid which either luminesced blue as in Figure 4 ($pH_{start} = 10.0$) or could not be activated to produce

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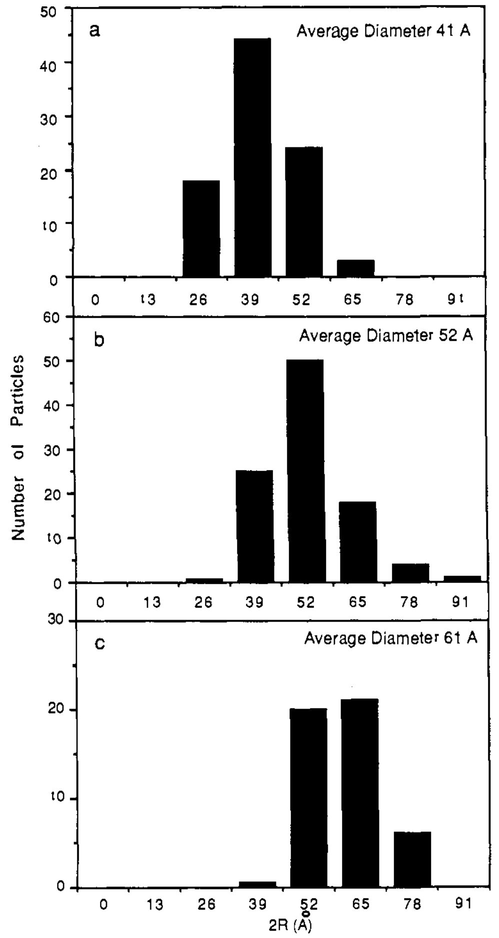

Figure 3. Histograms of three activated CdS colloids which were produced at pH_{start} = 9.8 (a), 9.0 (b), and 8.1 (c).

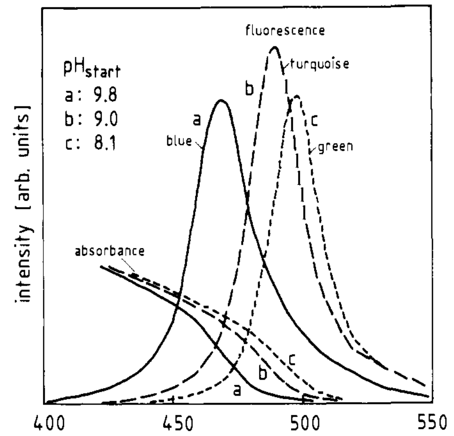

Figure 4. Absorption and fluorescence spectra of activated CdS. pH_{start} was 9.8 (a), 9.0 (b), and 8.1 (c).

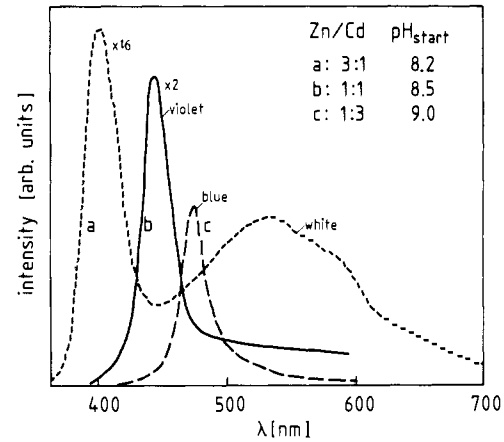

Figure 5. Fluorescence spectra of three activated ZnS/CdS co-colloids.

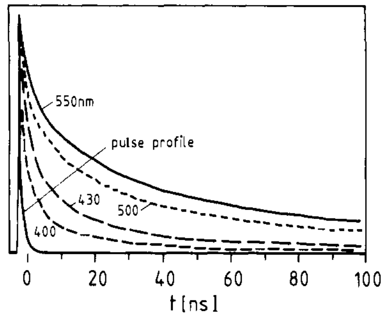

Figure 6. Fluorescence decay at different wavelengths of the activated colloid a of Figure 5. All curves normalized at t = 0.

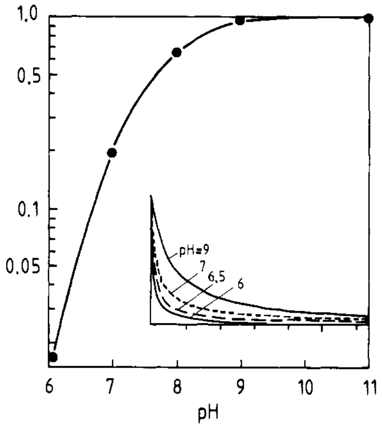

Figure 7. Fluorescence intensity of the activated colloid as a function of pH. Inset: Decay of the fluorescence at various pH values.

a narrow band (pH >10.0, see Figure 1). However, violet luminescing colloids were obtained by using co-colloids of CdS and ZnS instead of pure CdS as is reported in the following section.

Luminescence of CdS–ZnS Co-colloids. It has previously been shown that the simultaneous precipitation of Zn^{2+} and Cd^{2+} ions leads to a co-colloid, whose onset of absorption is continuously blue-shifted with increasing zinc content.[17]

Figure 5 shows fluorescence spectra of co-colloids which were activated by adding first NaOH to the base sol (to bring the pH up to 11.0) and then 6×10^{-4} M excess $Zn(ClO_4)_2$. The starting pH was between 8.2 and 9.0 as indicated in the figure. The maximum of the fluorescence band again appeared at the wavelength of the inflection point of the absorption spectrum. Blue and violet luminescing sols were obtained. Sol a in Figure 5 with a Zn/Cd ratio of 3:1 even produced a fluorescence band beginning in the ultraviolet. However, this sample luminesced with a white color due to the rather intense second fluorescence band which extended over the whole visible range of wavelengths.

The decay of the fluorescence at various wavelengths is shown by Figure 6 for the colloid with the ratio Zn/Cd = 3:1 (spectrum a in Figure 5). All decay curves were normalized at t = 0. The intensity decays in a multiexponential manner, the rate decreasing with increasing wavelength of observation. This behavior has previously been observed for pure ZnS[18] and CdS.[3b]

Luminescence of Activated CdS and pH of Solution. The solution of the activated CdS colloid (spectrum c in Figure 4) was

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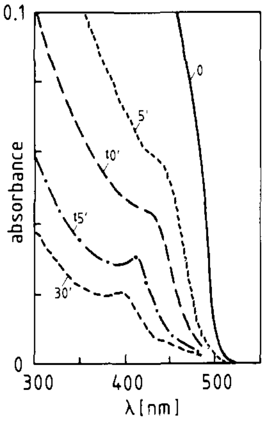

Figure 8. Absorption spectrum of nonactivated CdS in 2 × 10^{-4} M solution containing 2 × 10^{-4} M hexametaphosphate and air after different times of illumination.

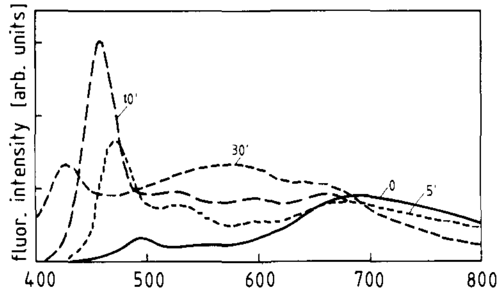

Figure 9. Fluorescence spectrum at different times of illumination of the CdS sol of Figure 8.

made more and more acidic by adding perchloric acid. Figure 7 shows how the intensity of the green luminescence changed with pH. Below pH 9, the intensity started to decrease rapidly. The inset of the figure shows the decay of the fluorescence at various pH values of the solution. The decay became substantially faster with decreasing pH. It was also observed that the absorption spectrum underwent small changes with pH. At pH 5, for example, the spectrum was less intense by 5% at all wavelengths. The intensity of absorption as well as the luminescence recovered partially after adjusting the pH back to 9.

Photoanodic Dissolution Experiments. Colloidal CdS dissolves in aerated solutions upon illumination:[1,2,10,19]

$$CdS + O_2 \xrightarrow{h\nu} Cd^{2+} + SO_4^{2-} \qquad (1)$$

As this reaction can be accelerated by certain solutes it has often been used as an indicator for studying the interaction of solutes with the charge carriers generated upon light absorption. In the present studies, such experiments were carried out to compare the stabilities of nonactivated and activated CdS sols.

Figure 8 shows how the absorption spectrum changed upon illumination of the nonactivated sol. As described previously, the onset of absorption was shifted toward shorter wavelengths and a weak maximum developed at about 50 nm below the onset (we regard as onset the wavelength which is obtained by extrapolating the steep part of the increase in absorption). As the colloidal particles became smaller during the photoanodic dissolution they showed typical size quantization effects. About half the CdS was consumed after 5 min in the experiments of Figure 8. The fluorescence spectrum of the particles also changed during the photoanodic dissolution. This is shown by Figure 9. Most remarkable is the formation of a relatively narrow band close to the onset of absorption as the particles become smaller. The maximum of the band shifted toward shorter wavelengths with increasing time of illumination. After 10 min this band decreased in intensity. At longer wavelengths, the broad band was slightly blue-shifted with increasing illumination time and increased in intensity. Similar observations have previously been made with CdS samples stabilized by silicon dioxide.[18] Figure 10 shows the effect of 1 × 10^{-4} M Tl^+ ions on the fluorescence spectrum, and Figure 11 shows how the rate of photoanodic dissolution was influenced by this additive. Tl^+ quenches the fluorescence, this effect being more pronounced at longer wavelengths than at shorter ones. Upon illumination, the sharp band at about 430 nm developed also in the presence of Tl^+ (Figure 10). The rate of photoanodic dissolution was strongly enhanced by Tl^+ ions (Figure 11). Silver ions, on the other hand, decreased the rate of dissolution by a factor of about 2. It should also be mentioned that the quantum yield of photoanodic dissolution (curve O in Figure 11) was 0.001 CdS molecules per photon absorbed. This yield is substantially lower than the yield of 0.03 observed previously for the dissolution of CdS stabilized by silicon dioxide.[1] Polyphosphate as stabilizer against the flocculation of the colloid also has a stabilizing effect against photodissolution.

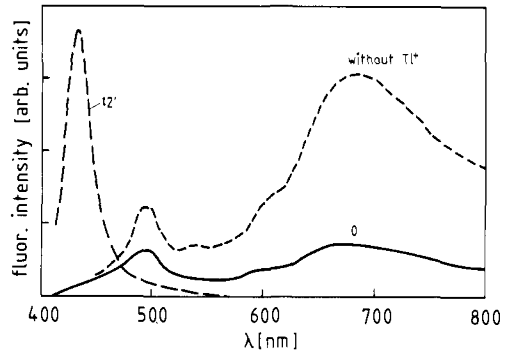

Figure 10. Spectrum of the nonactivated CdS sol without Tl^+: (0) spectrum after addition of 1 × 10^{-4} M $TlClO_4$; (12) spectrum after illumination for 12 min.

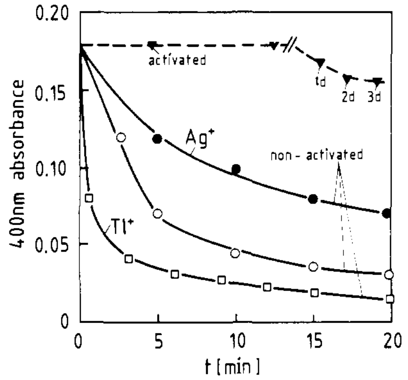

Figure 11. Photodissolution of 2 × 10^{-4} M nonactivated (full line) and of activated CdS (dashed). Absorbance at 400 nm as a function of illumination time. The solutions were saturated with oxygen. Tl^+ or Ag^+ were present at 1 × 10^{-4} M and 8 × 10^{-5} M, respectively.

The activated CdS colloid was very much more stable under illumination than the nonactivated one. This can also be seen from Figure 11. During irradiation times of about 10 min, where the nonactivated sample was photodissolved to a large extent, no sign of dissolution was observed for the activated probe. After 3 days of illumination a decomposition of 10% was detected. The absorbed photon concentration was 1 × 10^{-4} M s^{-1} in these experiments, and the particle concentration of CdS was 1.5 × 10^{-7} M. It is readily calculated that each particle had absorbed 1.7 × 10^8 photons after 3 days. The light stability of the activated colloid in aerated solution is comparable to that of organic dyes like Rhodamine 6G.

Colloidal CdS can also be degraded by OH radicals generated radiolytically in solutions containing nitrous oxide.[1] Such experiments were carried out with sol c (Figure 4) before and after activation. The nonactivated sol was almost completely degraded after a dose of 10^5 rads γ-radiation, while the activated one did

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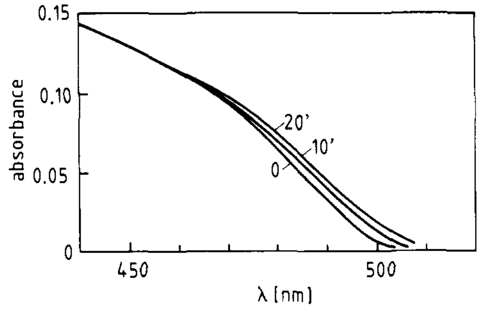

Figure 12. Absorption spectrum of deaerated activated CdS sol (c in Figure 4) before and after irradiation with a 3 Hz train of picosecond laser pulses. Absorbed photons: 2×10^{-5} M s^{-1}.

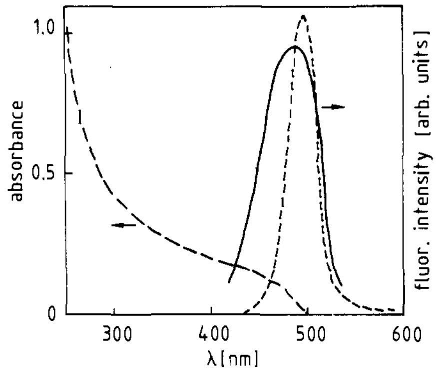

Figure 13. Absorption and fluorescence spectra of an activated CdS sol (dashed) and fluorescence spectrum as excited by a laser flash (full line). Excitation wavelength 366 nm for excitation in the fluorimeter and 355 nm for excitation by laser light.

not show any sign of decomposition.

Degradation and Fluorescence by Laser Excitation. A deaerated activated colloidal solution (spectrum c in Figure 4) was irradiated with a 3 Hz train of pulses from the picosecond laser (355 nm) during 10 min. The solution was stirred during illumination to expose all parts of the solution to the laser beam which irradiated a volume of 200 μL in the cell. The overall concentration of absorbed photons after this time was 1.2×10^{-2} M. The particle concentration being 1.5×10^{-7} M (mean agglomeration number 1300) one can calculate that each particle received 12000 photons under these conditions. While illumination with the light of a Xenon lamp did not produce any change in the absorption spectrum after this dose of absorbed photons, a small change was observed under the conditions of laser illumination. As is seen from Figure 12 the onset of absorption was slightly shifted to a longer wavelength. Additional illumination for 10 min caused the onset to shift further. These experiments show that photons are more effective in producing changes in the colloid when they are applied at high instantaneous intensity. However, the changes produced were not of the dissolution type of the above experiments as no decrease in the absorption at shorter wavelength (Figure 11) occurred. It seems that CdS particles were not degraded but simply increased in size under the laser illumination.

Figure 13 shows a comparison between the fluorescence spectra obtained (1) under the usual excitation conditions in the fluorimeter and (2) under excitation by a flash of the picosecond laser. It is recognized that the fluorescence band was slightly blue-shifted and broadened under the conditions of laser excitation. The fluorescence lifetime was 50 ns in the case of low illumination intensity and shorter than 50 ps in the case of laser excitation.

More drastic changes occurred upon irradiation of the colloidal solution with focussed light of the laser flashes, when the intensity was so high that each CdS molecule absorbed about 100 photons per laser flash. Figure 14 shows the absorption spectra before and after illumination during 10 min, both in the presence and in the absence of air. In the absence of air an increase in absorption at almost all wavelengths was observed. After exposing the irradiated solution to air, this absorption decreased by about 30%. These changes are typical for the formation of Cd metal on the colloidal particles.[20] It is concluded that extremely high light intensity causes a chemical decomposition of the colloidal particles which, however, is different from the photoanodic dissolution described above (Figure 8). In the presence of air a strong decrease in the absorption spectrum of CdS was observed which is interpreted as an anodic dissolution process.

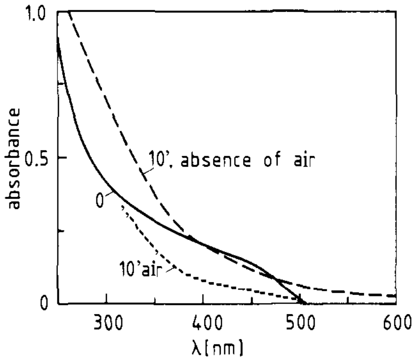

Figure 14. Absorption spectrum of an activated colloid before and after 10 min of illumination with 3 Hz trains of focussed laser pulses in the absence and presence of air.

Discussion

Particle Size and Absorption. It is important from the point of view of colloid preparation that conditions have been found under which yellow CdS sols of different mean particle size and relatively narrow size distribution can be made. The crucial factor in the preparation is the starting pH value which must lie in the range between 6.5 and 10.0. Colloids produced in this way can be recovered as redissoluble solids. Moreover the mean size can be controlled by the starting pH in the above critical range. The higher the pH the smaller are the particles. The size of the particles is in the range between 60 and 40 Å where the blue-shift of the onset of absorption becomes noticeable.

In our previous studies, CdS samples of quite different mean size were prepared and the onset of absorption determined. A curve describing λ_{thres} (wavelength of absorption threshold) as a function of the diameter of the particles resulted from these studies.[14] The samples in the range from 40 to 60 Å were not prepared under the present conditions, i.e., they had a wider size distribution, which caused certain uncertainties in the determination of the threshold. On the basis of our present data, taking as threshold the inflection point of the absorption spectrum, the new curve in Figure 15 resulted. The figure also contains our older curve. It can be seen that the size quantization effects are more pronounced for the larger particle sizes than they previously appeared to be. It should also be mentioned that the new curve agrees very well with a quantum mechanical calculation, in which the electron-hole pair was treated as one body by using a hydrogen atom like wave function and a potential jump of 3.8 eV at the particle–solution interface.[14] The stronger dependence of λ_{thres} on size is in better agreement with the simple expectation that the blue-shift of the absorption should already become noticeable as the size of a CdS particle falls below the 60 Å diameter of an exciton in macrocrystalline CdS.[13]

Activation of Fluorescence. The CdS colloids generally have a weak broad emission ranging from 500 to 700 nm. This fluorescence is attributed to the recombination of charge carriers immobilized in traps of different energies. The low quantum yield, generally less than 1%, of this fluorescence is taken as an indication that radiationless recombination of the charge carriers is the dominating process of their disappearance. The activation of the colloid simply consists of a precipitation of cadmium hydroxide on the CdS sol. One can only speculate at the present time about the mechanism of this activation. At the high pH, SH^- groups

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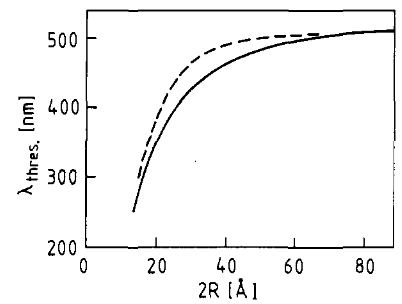

Figure 15. Wavelength of absorption threshold of CdS as a function of particle diameter (dashed: previous work).[14]

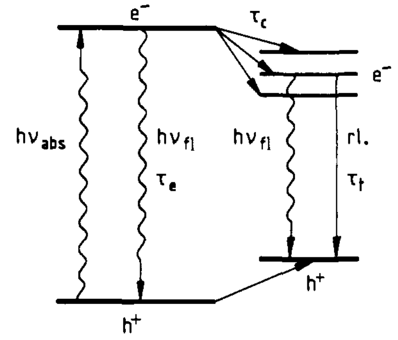

Figure 16. Scheme of absorption and fluorescence in small colloidal CdS particles (rl: radiationless transition).

of the surface of the colloidal particles are converted into S^{2-} ions which then bind excess Cd^{2+} ions, possibly in the form of $S^{2-}\cdots Cd^{2+}\cdots OH^-$ structures. The removal of SH^- groups and the accumulation of Cd^{2+} on the surface thus seem to destroy the sites where radiationless recombination of the charge carriers can occur.

The nonactivated colloids could be recovered as redissoluble solids. Activation of the redissolved particles also was possible. Further, the activated samples could be recovered again as solids which showed a strong green luminescence.

The activation has two effects: (1) the long wavelength fluorescence of the nonactivated colloid is slightly increased and (2) a very strong fluorescence at the onset of absorption appears. The new fluorescence band is attributed to the recombination of charge carriers either before they are trapped (band gap recombination) or while they are trapped in very shallow traps (near band gap recombination). The fluorescence close to the band gap energy decays with first half-lifetimes longer than 10 ns, and it is this relatively long lifetime which makes us believe that this fluorescence is not due to band gap recombination but to a process where the lifetime of the charge carriers is increased by weak trapping (less than 0.1 eV trap depth). The blocking of defect sites as described above is a typical problem in the photoelectrochemistry of semiconductor electrodes. "Deep centers with energy levels closer to the center of the forbidden gap most efficiently bridge the valence and conduction bands causing radiationless relaxation".[21] The picture which now emerges is illustrated by Figure 16. Light absorption leads to an e^-–h^+ pair or exciton which either undergoes radiative band gap or near band gap recombination with a characteristic time τ_e or crossover into traps of various energies with time τ_c. The recombination from these states takes place with a much longer time τ_t. In the nonactivated colloids, τ_t is mainly determined by the radiationless process. In the activated colloids the number of traps is strongly reduced. τ_c becomes longer than τ_e, i.e., near band gap fluorescence is the predominant process of recombination. The nature of the few remaining deeper traps is also changed, i.e., radiative recombination is much more frequent than before activation. Thus, despite of the smaller number of traps, emission of light from trap recombination is more intense than before activation.

When the activated colloidal solution was brought to pH values lower than 9.0, the fluorescence intensity of the narrow band decreased rapidly and the rate of the decay became faster (Figure 7). It seems plausible to interpret this finding in terms of a gradual dissolution of the layer of cadmium hydroxide which had been produced upon activation.

Photoanodic Dissolution. The mechanism of photoanodic dissolution of CdS in the presence of oxygen has previously been clarified. Oxygen acts as an acceptor of the electrons which are generated by light absorption and also as a scavenger of the positive holes that remain. It is this double action of oxygen which makes the dissolution rather efficient in the presence of this solute. Other electron acceptors such as methyl viologen did not promote the photoanodic dissolution in the absence of oxygen but accelerate the reaction substantially in its presence.[1,2,10,12,19]

Photodissolution of the nonactivated colloid is accompanied by interesting changes in the fluorescence properties of the particles. As they become smaller they luminesce stronger and also develop the narrow fluorescence band close to the absorption threshold, i.e., photoanodic dissolution has, to a certain extent, the same effect as activation by precipitation of cadmium hydroxide. According to the picture discussed above it is concluded that the defect sites on the surface of the particles that catalyze the radiationless recombination of charge carriers are reduced upon photoanodic dissolution. This could simply be due to the fact that excess Cd^{2+} ions are formed during the dissolution which precipitate as a hydroxide layer in the alkaline solution. It could also be that the photoanodic dissolution occurs preferentially at the defect sites. Tl^+ ions promote the photoanodic dissolution and efficiently quench the fluorescence at longer wavelengths. They are less effective in quenching the new band gap fluorescence (Figure 10). The action of Tl^+ is attributed to the scavenging of electrons generated by light absorption: $Tl^+ + e^- \rightarrow Tl^0$. In the presence of oxygen, reoxidation of Tl^0 occurs, Tl^+ thus acting simply as an electron relay in the photoanodic dissolution of CdS.[1]

The strong luminescing sols could become inorganic substitutes for organic dye solutions in various applications. In this respect it was interesting to study the stability of the colloids toward illumination. The stability toward anodic dissolution under ordinary illumination conditions with a xenon lamp is 2000 times greater after activation (Figure 11). As already mentioned above, a crucial step in the photoanodic dissolution is the reaction of oxygen with surface trapped positive holes which chemically are S^- radical anions. The great stability of the activated colloids is attributed to the fact that the sulfur sites on the surface are no longer accessible to O_2 molecules due to the cadmium hydroxide layer. The same explanation holds for the stability of the activated colloid toward attack by OH radicals.

Laser-Induced Decomposition. The changes in colloidal CdS which are produced by intense laser flashes are quite different from the above photoanodic dissolution upon illumination with the light of a xenon lamp. The changes in Figure 12 are not attributed to chemical changes but simply to an increase in the size of the particles. During the picosecond laser flash a large number of photons are absorbed. This leads to certain changes in the optical absorption during the flash itself which will be described in a forthcoming paper. The absorbed energy is finally accumulated in the particle in the form of heat, and the temperature rise, although existing only for a short time, is believed to eject Cd^{2+} and S^{2-} ions from the surface into the solution. These fragments then settle down on CdS particles, the whole effect being an acceleration of the Ostwald ripening which always takes place in colloidal solutions.

A chemical decomposition, however, was observed in the experiments of Figure 14. The intensity of the focussed laser was so high that at least 100 times more photons were absorbed in one particle as CdS molecules were present in it. Under these conditions, a plasma of electrons and holes must exist in the particle during the short time of the laser flash, and it does not seem surprising that decomposition into the elements Cd and S

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takes place under these extreme conditions. In the presence of air, the Cd atoms were reoxidized to Cd^{2+}, the overall process thus being an anodic corrosion.

The near band gap fluorescence was slightly blue-shifted when excited by intense laser light (Figure 13). Under these circumstances, the emission did not occur from a particle carrying just one e$^-$–h$^+$ pair but had been excited by several photons at the same time. The energy level of the exciton in a small CdS particle carrying one or two excess electrons is shifted to shorter wavelengths.[22] We invoke this effect in our explanation of the blue-shift in Figure 13. The extremely short lifetime of the fluorescence upon laser excitation is explained by the strongly increased rate of recombination of the charge carriers due to the high local concentration during the flash.

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Molybdenum(VI) and Molybdenum(V) Complexes with *N*,*N'*-Dimethyl-*N*,*N'*-bis(2-mercaptophenyl)ethylenediamine. Electrochemical and Electron Paramagnetic Resonance Models for the Molybdenum(VI/V) Centers of the Molybdenum Hydroxylases and Related Enzymes

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Abstract: As models for the molybdenum(VI/V) centers of the molybdenum hydroxylases and related enzymes, MoO$_2$L and MoOClL (LH$_2$ = *N*,*N'*-dimethyl-*N*,*N'*-bis(2-mercaptophenyl)ethylenediamine) have been synthesized. The structure of MoO$_2$L has been determined by X-ray crystallography. The compound crystallizes in space group $P2_1/n$, with a = 10.049 (2) Å, b = 14.538 (2) Å, c = 12.143 (1) Å, β = 103.73 (1)°, and Z = 4. MoO$_2$L is six-coordinate with approximate C_2 symmetry, with the two thiolate S atoms trans to one another and the two tertiary amine N atoms approximately trans to the terminal oxo groups. MoO$_2$L undergoes reversible one-electron reduction on both the cyclic voltammetric and coulometric time scales to give various oxo–Mo(V) complexes. The EPR spectra of these complexes, including ^{98}Mo, ^{2}H, and ^{17}O substituted species, are consistent with formulation as [MoO$_2$L]$^-$, *cis*-MoO(OH)L, [MoOSL]$^-$, and *cis*-MoO(SH)L. ^{1}H coupling constants for *cis*-MoO(OH)L (1.65 mT) and *cis*-MoO(SH)L (1.05 mT) and the ^{17}O coupling constants for Mo^{17}O(^{17}OH)L (0.25 and 0.82 mT), [Mo^{17}OSL]$^-$ (0.43 mT), and Mo^{17}O(SH)L (0.22 mT) have been measured. MoOClL exhibits reversible one-electron electrochemical reduction in its cyclic voltammogram but decomposes upon coulometric reduction. EPR data indicate it is *trans*-MoOClL. Substitution of Cl$^-$ by OH$^-$, F$^-$, and SH$^-$ has been effected in solution. The implications of the results for the structures of Mo(VI/V) centers of the enzymes are discussed. In particular, Mo^{V}OS(OR) and Mo^{V}O(SH)(OR) (OR = bound product) are suggested as the centers responsible for the "very rapid" and "rapid" EPR signals of xanthine oxidase. An Mo^{V}O(OH) center appears to be involved in the "slow" EPR signal of xanthine oxidase and the low pH forms of sulfite oxidase and nitrate reductase; the high pH forms of the latter enzymes, however, do not appear to involve a conjugate base Mo^{V}O$_2$ center.

The molybdenum hydroxylases and related enzymes catalyze biological two electron redox reactions in which an oxygen atom or a hydroxyl group is added to or removed from the substrate. The most extensively studied of these enzymes are xanthine oxidase (XO),[2a] xanthine dehydrogenase (XD),[3a] sulfite oxidase (SO),[2a] and nitrate reductase (NR).[2b] The minimal structure of the molybdenum center, as deduced by EXAFS and EPR investigations, for oxidized XO and XD is Mo^{VI}O(S)(SR)$_2$,[3] with an oxo, sulfide, and two thiolate ligands. A Mo^{VI}O$_2$(SR)$_{2-3}$ center with two oxo and two or three thiolate ligands appears to be present in oxidized SO, in the desulfo form of XD and in oxidized NR from *Chlorella vulgaris*.[3a] Some of the thiolate ligands may be furnished by the molybdenum cofactor, Mo-co.[4] Oxygen, ni-

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