

Absorption and Fluorescence Behavior of Redispersible CdS Colloids in Various Organic Solvents

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For the first time, redispersible CdS colloids with a narrow size distribution were prepared which readily dissolve in a wide range of polar and nonpolar organic solvents. The absorption and fluorescence properties of these CdS colloids stabilized with sulfonic acids were studied as a function of both the dielectric constant and hydrogen bonding ability of the solvent. The absorption spectra of the CdS colloids, reflecting their particle size distribution, are not affected by the solvent, but their fluorescence behavior is strongly solvent dependent. In protic solvents, only trapped emission is observed whereas both excitonic and trapped fluorescence occur in aprotic solvents, the intensity of the emission depending on the dielectric constant of the aprotic solvent. Furthermore, the sulfonic acid bound to the CdS particle surface could be exchanged for other stabilizers such as polyphosphate, silicate, 2-mercaptoethanol, 3-mercapto-1,2-propanediol, and benzenethiol. Stabilizer exchange drastically changes the solubility and the fluorescence of the CdS particles but has no significant effect on their absorption spectra.

Introduction

Within the last years small semiconductor particles with sizes in the nanometer range have been extensively studied.¹⁻³ The size-dependent confinement of the charge carriers in these quantum crystallites leads to drastical changes in their optical and catalytic properties compared to those of the bulk semiconductor.¹⁻⁴ However, the relatively broad particle size distribution of most colloids complicates the quantitative correlation of the physical and chemical properties of the semiconductor with the crystallite size. The investigation of these size-dependent properties thus requires the rigorous control of both the semiconductor particle size and dispersity. New methods for preparing and isolating semiconductor crystallites with a narrow particle size distribution have been recently developed involving the synthesis of particles in vesicles,⁵ zeolites,⁶ glasses,⁷ and polymers,⁸ surface modification procedures,^{9,10} biosynthesis,¹¹ and separation (according to size) by chromatography.¹²

The fluorescence behavior of small semiconductor

particles has been intensively studied in order to obtain information on the energetics and dynamics of photogenerated charge carriers as well as on the nature of the emitting states.^{9b,13-16} Whereas in a macrocrystal charge carriers are trapped at defect sites or doping ions in the bulk, in small particles, these traps are most likely located at the surface.^{15,16} Therefore, in these small crystallites, the trapped charge carriers at the surface feel not only the continuum of the crystal but also the presence of molecules or ions, i.e., stabilizer, solvent or solute molecules interacting with the particle surface.¹⁶ For a certain particle size distribution, both the spectral position and yield of the crystallite fluorescence can thus be modified by changing the chemical nature of the colloid surface.^{9a,b,15,16} Covering the surface of weakly red emitting CdS with cadmium hydroxide yields strongly fluorescing particles with a sharp emission band at the absorption onset.^{9b} The spectral position of this fluorescence, i.e., the negligible Stokes shift, suggests that it is due to the radiative recombination of free charge carriers or excitonic fluorescence.^{9b,16} Furthermore, it is known that the trapped emission of colloidal CdS can be drastically enhanced by the addition of methanol.¹⁷

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We report here the dependence of the optical properties of colloidal CdS on both the solvent, i.e., its dielectric constant and hydrogen bonding ability, and the stabilizing agent. We were particularly interested in obtaining information about the nature of the emitting states and determining the effect of the stabilizing agent on the optical properties of the colloid. The solvent and stabilizer dependence of the optical properties of CdS have not yet been systematically studied before since such an investigation requires the preparation of a CdS colloid which both dissolves in a broad variety of organic solvents and allows stabilizer exchange to occur without changing its particle size distribution. A prerequisite for this work is thus the preparation of CdS colloids with a narrow particle size distribution which dissolve in various polar and nonpolar organic solvents. Ideally, the particle size distribution of these colloids should be insensitive to both the solvent and the stabilizer.

Experimental Section

Preparation of the CdS Colloid. Injection of 11 mL of H_2S (2×10^{-3} M) into 250 mL of 1-propanol (spectroscopic grade) containing 2.2×10^{-3} M $\text{Cd}(\text{ClO}_4)_2$ (Alfa) and 5×10^{-3} M sulfonic acid led to the formation of a yellow CdS colloid. The following sulfonic acids (or their sodium salts) were used as stabilizers: toluene-4-sulfonic acid (Merck), (1S)-(+)-camphor-10-sulfonic acid monohydrate (Merck), 5-sulfosalicylic acid dihydrate (Merck), sodium 1-hexanesulfonate (Aldrich), sodium 4-dodecylbenzenesulfonate (Fluka), and sodium 3-(trimethylsilyl)propane-sulfonate (Merck). In the case of the sodium salts, HClO_4 (5×10^{-3} M) was added to the solution yielding the corresponding sulfonic acid. Ripening of the colloids occurred within 2 days yielding 2×10^{-3} M CdS solutions which were stable for weeks. The rather steep absorption onset of these colloids suggests a narrow particle size distribution. All the experiments described in the following sections were carried out with CdS colloids stabilized with 4-dodecylbenzenesulfonic acid.

The fluorescence of the CdS colloids was activated by diluting (1:1) the 2×10^{-3} M CdS stock solution with 5×10^{-3} M cadmium 2-ethylhexanoate (Strem Chemicals) in 1-propanol. Solutions of activated CdS thus contained 1×10^{-3} M CdS and 2.5×10^{-3} M cadmium 2-ethylhexanoate. Evaporation of the solvent with a rotavapor at 30–35 °C yielded redispersible CdS powders which readily dissolved in various aliphatic alcohols, chlorinated solvents, diethyl ether, acetone, *n*-hexane, toluene, DMF, and DMSO. However, the CdS powders were insoluble in water, methanol, ethanol, and acetonitrile.

Stabilizer Exchange. The stabilizing 4-dodecylbenzenesulfonic acid could be exchanged for sodium polyphosphate (Riedel-de-Haen), sodium silicate (Merck), 2-mercaptoethanol (Merck), 3-mercapto-1,2-propanediol (Fluka), and benzenethiol (Sigma). In the case of sodium polyphosphate or silicate, the CdS powder was dissolved in an aqueous solution containing 1×10^{-2} M sodium polyphosphate or silicate. In the case of 2-mercaptoethanol and 3-mercapto-1,2-propanediol, an aqueous solution containing 1×10^{-2} M thiol was added to an activated CdS powder. The turbid solution (pH = 4.0) turned clear when its pH value was increased above 8.0 (2-mercaptoethanol) or 9.0 (3-mercapto-1,2-propanediol). For benzenethiol, stabilizer exchange was carried out by diluting an activated CdS solution with acetonitrile (1-propanol/acetonitrile (1:4)) and adding 1×10^{-2} M benzenethiol and 2×10^{-2} M NaOH. The solvent was evaporated and the resulting powder redissolved in acetonitrile. The fact that the exchange of the stabilizing sulfonic acid for a polyphosphate, silicate, or thiol was successful was supported by the corresponding change in solubility of the CdS colloid.

Methods. Absorption spectra of the CdS colloids were measured on an Omega 10 spectrophotometer (Bruins Instruments) with 1-nm resolution and were obtained by averaging three spectra. Fluorescence spectra were recorded on a self-made fluorometer consisting of a 450-W Xe lamp in combination with a GCA McPherson monochromator as excitation light source and a Spex double monochromator, type 1672, with a single

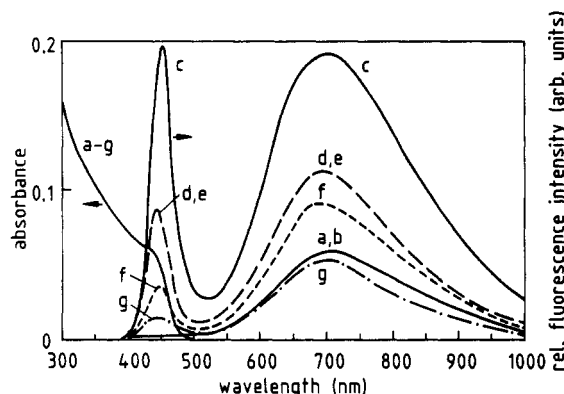


Figure 1. Absorption and fluorescence spectra of colloidal CdS stabilized with 4-dodecylbenzenesulfonic acid in various protic and aprotic solvents: 1-propanol (a), 1-octanol (b), CCl_4 (c), *n*-hexane (d), CHCl_3 (e), CH_2Cl_2 (f), and acetone (g). Absorbance in 5-mm cell.

photon counting detector in the UV-VIS-emission path and a Spex 1681 monochromator together with a Ge detector (North Coast Scientific Instruments) in the near-IR region. All the signals were digitized and the data was processed with a PDP 11/23 minicomputer. The emission spectra were corrected for the spectral response of the measuring system. Excitation was at 360 nm and all the fluorescence spectra were recorded at the same optical density of 0.16 at 360 nm. Photolysis of activated CdS colloids was carried out in air-saturated solution with a 1000-W Xe lamp (Photon Technology International Inc.). Transmission electron micrographs (TEM) were recorded on a Philips CM 12 transmission electron microscope. For the preparation of the samples, one droplet of a CdS solution was placed on a copper grid covered with a carbon support film, and the solvent was evaporated.

Results and Discussion

TEM, Absorption, and Fluorescence of Colloidal CdS in Organic Solvents. Preparation of colloidal CdS in 1-propanol with 4-dodecylbenzenesulfonic acid as stabilizer yields cubic CdS particles with a narrow particle size distribution and a mean particle diameter of 39 Å. The absorption spectrum of such a CdS colloid is shown in Figure 1. The same absorption spectra with an excitonic transition at 445 nm are obtained for all sulfonic acids, indicating similar particle size distributions. The insensitivity of particle size toward the nature of the stabilizing sulfonic acid suggests a thermodynamically preferred size distribution.

As also shown in Figure 1, the absorption spectrum of colloidal CdS is solvent independent, but its fluorescence is strongly affected by the solvent. In protic solvents, only a weak red emission at ca. 700 nm is observed, but in aprotic solvents, both a violet fluorescence at ca. 450 nm and a red fluorescence at ca. 700 nm occur. The Stokes-shifted red fluorescence band at 700 nm arises from the radiative recombination of trapped charge carriers, whereas the violet fluorescence band at ca. 450 nm is attributed to excitonic fluorescence. It has been shown for colloidal CdS that the excitonic fluorescence most likely arises from the radiative recombination of thermally detrapped electrons with valence band holes.^{16a,b,18} Fluorescence excitation and absorption spectra of the CdS colloids are in good agreement indicating both a narrow particle size distribution and a contribution of all the particle sizes to the observed fluorescence.

The occurrence of the fluorescence bands clearly depend on the hydrogen bonding ability of the solvent but is

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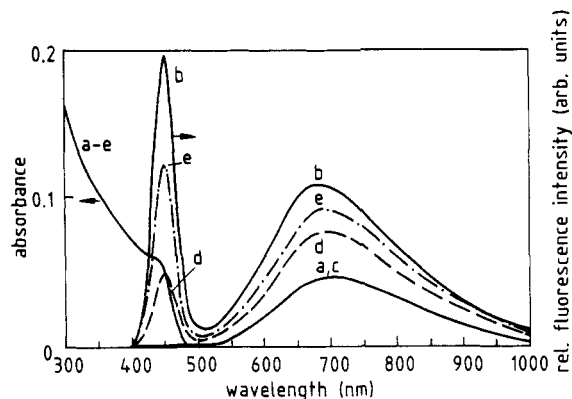


Figure 2. Absorption and fluorescence spectra of CdS after solvent exchange: 1-propanol (a), sample a redissolved in CCl_4 (b), sample b redissolved in 1-propanol (c), sample c redissolved in CCl_4 (d), and sample d after 3 days (e).

independent of its (static) dielectric constant (ϵ), as can be seen from the fluorescence spectra in Figure 1; in protic solvents such as 1-propanol ($\epsilon = 20.1$, spectrum a)¹⁹ and 1-octanol ($\epsilon = 10.3$, spectrum b)¹⁹ only trapped emission is observed, whereas in aprotic solvents such as acetone ($\epsilon = 20.7$, spectrum g),¹⁹ CH_2Cl_2 ($\epsilon = 9.08$, spectrum f),¹⁹ CHCl_3 ($\epsilon = 4.81$, spectrum e),¹⁹ CCl_4 ($\epsilon = 2.24$, spectrum c),¹⁹ and *n*-hexane ($\epsilon = 1.89$, spectrum d)¹⁹ both excitonic and trapped fluorescence occur. Furthermore, in aprotic solvents, the fluorescence intensity is affected by the solvent dielectric constant in such a way that an increase in dielectric constant seemingly leads to a decrease in fluorescence intensity. In aprotic solvents with a high dielectric constant such as DMF ($\epsilon = 36.71$)¹⁹ and DMSO ($\epsilon = 46.68$),¹⁹ no measureable fluorescence is found. In protic solvents, the fluorescence intensity is independent of the dielectric constant, Figure 1.

Exchanging a protic for an aprotic solvent and vice versa results in more or less reversible changes in the spectral position of the fluorescence bands as shown in Figure 2. The exchange of 1-propanol for an aprotic solvent such as CCl_4 leads to both violet and red fluorescence. The violet fluorescence disappears upon exchange of CCl_4 for 1-propanol but reappears with a lower yield when the protic 1-propanol is substituted for the aprotic CCl_4 . Aging of this CdS solution in the dark leads to an increase in intensity of both the excitonic and trapped fluorescence. Similar results are obtained with CH_2Cl_2 as aprotic and both 1-octanol and 1-decanol ($\epsilon = 8.1$)¹⁹ as protic solvents indicating that the spectral position of the fluorescence band depends on the hydrogen bonding ability of the solvent but not on its dielectric constant.

As shown in Figure 3, addition of a protic solvent such as 1-propanol to a solution of CdS in an aprotic solvent such as *n*-hexane (water content, $5 \times 10^{-3}\%$) leads to a strong decrease of the excitonic fluorescence, but the intensity of the trapped emission is not affected. Furthermore, addition of small amounts of water or gaseous HCl to a CdS colloid in diethyl ether (water content, $<1 \times 10^{-2}\%$) also strongly quenches the excitonic fluorescence of the colloid. However, even in 1-propanol containing less than $1 \times 10^{-3}\%$ water, no excitonic fluorescence is observed. Thus, we could exclude that the absence of the excitonic fluorescence of CdS in protic solvents is merely caused by the higher water content of these aliphatic alcohols compared to that of aprotic solvents.

The fluorescence quenching experiments suggest that the excitonic fluorescence of colloidal CdS is only observed

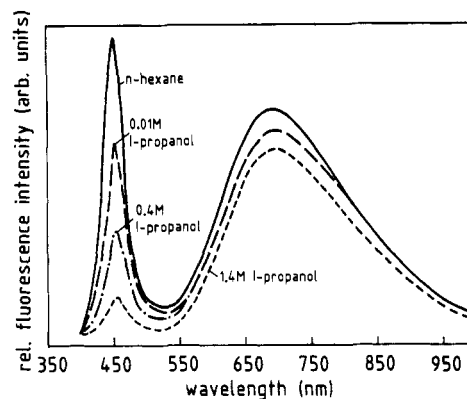


Figure 3. Fluorescence spectra of CdS in *n*-hexane before and after addition of various amounts of 1-propanol.

in the absence of solvent or solute molecules forming hydrogen bonds to the sulfur anions at the surface of the CdS particles. It has been shown for CdS in aqueous solution that the hole traps are most likely located at the sulfur anions at the particle surface.²⁰ Similarly, the fluorescence of CdS colloids strongly depends on the pH of the aqueous solution; excitonic fluorescence is only observed at pH values above 6, its intensity strongly increasing with increasing pH. Under these conditions, the surface of the CdS particles is more or less covered with cadmium hydroxide.^{9b} Binding of the sulfur anions to cadmium hydroxide seemingly blocks the hole traps, thus leading to excitonic fluorescence.^{9b} At lower pH values, where the sulfur anions are protonated, only trapped emission occurs suggesting the existence of hole traps under these conditions. For CdS colloids in organic solvents, a similar mechanism may be operative; in protic solvents, hydrogen bonds could be formed to the sulfur anions at the particle surface leading to trapped emission, whereas in aprotic solvents some hole traps seem to be blocked by binding to cadmium ions, i.e., both excitonic and trapped fluorescence occur.

In aqueous solution, excitonic fluorescence is only observed in the presence of both excess cadmium and hydroxide ions, whereas in organic solvents, both the presence of excess cadmium ions and the absence of hydrogen bonds are essential. A prerequisite for the observation of excitonic fluorescence, i.e., for the blocking of hole traps, thus seems to be binding of the sulfur anions at the CdS particle surface to excess cadmium ions.²¹ In aqueous solution, the strength of this S-Cd bond depends on the pH, whereas in organic solvents, it is influenced by hydrogen bonds. Both the protonation of the sulfur anions in aqueous solution at low pH values or in protic solvents, and the formation of hydrogen bonds to the sulfur anions seem to considerably weaken the S-Cd bond. Thus, under these conditions, only trapped emission is observed.

Photolysis of CdS in Various Solvents. Photolysis of CdS colloids in various protic and aprotic solvents leads to a decrease in optical density, but the shape of the absorption spectrum and, thus, the particle size distribution remain unaffected. This suggests a thermodynamically preferred particle size distribution. As shown in Figure 4, the yield of photocorrosion clearly depends

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(21) The dissociation constant of cadmium 2-ethylhexanoate which was added in order to activate the fluorescence of the CdS colloids depends on the dielectric constant of the solvent. In polar solvents, this cadmium source more or less dissociates into ions, but in nonpolar solvents the molecular species is more likely. Thus, in polar solvents, the sulfur anions bind to cadmium ions whereas in nonpolar solvents, they bind to non-dissociated cadmium species.

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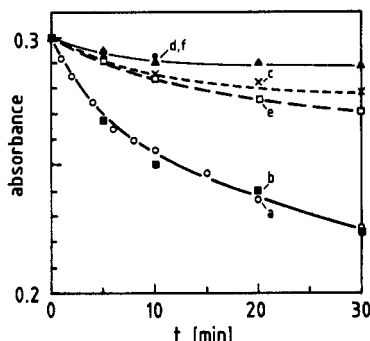


Figure 4. Photolysis of activated CdS colloids in various protic and aprotic solvents under air: 1-propanol (a), 1-octanol (b), CCl_4 (c), *n*-hexane (d), CHCl_3 (e), CH_2Cl_2 (f).

on the hydrogen bonding ability of the solvent. In aprotic solvents where both excitonic and trapped fluorescence are noticed, the photodecomposition of CdS is significantly slower than in protic solvents where only trapped emission occurs. A similar behavior has been observed for colloidal CdS in aqueous solution;^{9b} at high pH values, i.e., under conditions where excitonic fluorescence arises, the CdS particles are very stable toward photodecomposition. However, at low pH values, where only trapped emission is observed, photocorrosion is much faster. This suggests that the photocorrosion of CdS preferentially occurs at hole trap sites at the particle surface; i.e., under conditions where some hole traps are blocked, the yield of photodecomposition is accordingly reduced. Similar conclusions have already been drawn following a pulse radiolysis study in which trapped holes were identified as precursors for the photocorrosion.²²

Stabilizer Exchange. The stabilizing 4-dodecylbenzenesulfonic acid could be exchanged for sodium polyphosphate, sodium silicate, 2-mercaptoethanol, 3-mercapto-1,2-propanediol, or benzenethiol. The exchange of the stabilizing sulfonic acid for polyphosphate, silicate, or thiol is suggested by the corresponding change in solubility of the CdS colloid. In the case of sodium polyphosphate, silicate, 2-mercaptoethanol, and 3-mercapto-1,2-propanediol, stabilizer exchange results in a water-soluble colloid, whereas for benzenethiol, stabilizer exchange leads to CdS particles which readily redissolve in acetonitrile. CdS stabilized with 4-dodecylbenzenesulfonic acid dissolves in neither water nor acetonitrile.

The absorption and fluorescence spectra of the resulting CdS colloids containing excess cadmium ions are shown in Figure 5. Stabilizer exchange does not seemingly affect the absorption properties of colloidal CdS, suggesting that the stabilizer does not contribute to the absorption. However, the stabilizer clearly influences the fluorescence behavior of CdS. For sodium silicate, 2-mercaptoethanol, 3-mercapto-1,2-propanediol, and sodium polyphosphate at pH 5, only red emission is observed, its intensity depending on the stabilizer. However, for sodium polyphosphate at pH 11, both excitonic and trapped fluores-

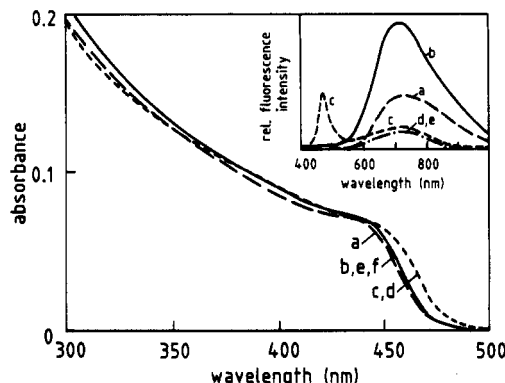


Figure 5. Absorption and fluorescence spectra of CdS before and after stabilizer exchange: 4-dodecylbenzenesulfonic acid, 1-propanol (a), 1×10^{-2} M polyphosphate, H_2O , pH = 5 (b), 1×10^{-2} M polyphosphate, H_2O , pH = 11 (c), 1×10^{-2} M 2-mercaptoethanol, H_2O , pH = 11 (d), 1×10^{-2} M 3-mercapto-1,2-propanediol, H_2O , pH = 11 (e), and 1×10^{-2} M benzenethiol, acetonitrile (f).

cence occur consistent with the previously proposed fluorescence model.^{9b} In the case of benzenethiol, no detectable emission is observed.^{10d}

Conclusions

By use of sulfonic acids as stabilizing agents, CdS colloids with a narrow particle size distribution could be prepared which readily dissolve in a broad variety of polar and nonpolar organic solvents. The absorption spectra of these colloids and thus their particle size distribution are solvent independent. However, their fluorescence behavior is clearly affected by the nature, i.e., the hydrogen bonding ability of the solvent; in protic solvents, only trapped emission occurs whereas both excitonic and trapped fluorescence are observed in aprotic solvents. Furthermore, in aprotic solvents addition of solute molecules capable of hydrogen bond formation strongly quenches only the excitonic fluorescence. This suggests that under conditions where hydrogen bonds can be formed to the sulfur anions at the particle surface, only trapped emission is observed. In aprotic solvents where both excitonic and trapped fluorescence occur, some hole traps seem to be blocked by binding of the sulfur anions to cadmium ions.²¹ Similarly, the yield of photocorrosion of CdS depends on the hydrogen bonding ability of the solvent; in aprotic solvents where hole traps seem to be blocked, the photodecomposition of CdS is significantly slower than in protic solvents.

The stabilizing sulfonic acid bound to the particle surface could be exchanged for polyphosphate, silicate, and various thiols as indicated by a corresponding change in solubility of the CdS powder. Stabilizer exchange does not significantly affect the absorption properties of colloidal CdS but clearly modifies the particle surface, thus changing the solubility of the colloid and its fluorescence behavior.

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