

Photoluminescence and Photoinduced Oxygen Adsorption of Colloidal Zinc Sulfide Dispersions

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Three distinct photoluminescence bands have been observed upon irradiation of doped and undoped ZnS colloidal semiconductor dispersions with ultraband gap light. Two blue emissions (BL1, $\lambda_{\max} = 428$ nm; and BL2, $\lambda_{\max} = 418$ nm) are attributed to sulfur vacancy and interstitial sulfur lattice defects, respectively. Growth of an efficient orange luminescence (OL) due to Mn^{2+} doping ($\lambda_{\max} = 583$ nm, $\phi = 0.08$ for 5% doping) was observed; the intensity of this emission depended on the dopant concentration in ZnS, the presence of dissolved oxygen, and the absence of dissolved sulfide ion in solution. A lowering of the oxygen concentration upon ultra band gap irradiation of the ZnS is attributed to photoassisted adsorption on the particle surface. The OL emission was quenched effectively by $\text{S}_2\text{O}_8^{2-}$ and HS^- but not by $\text{C}_2\text{O}_4^{2-}$, phenol, or OH^- .

Introduction

Colloidal semiconductor suspensions are useful in the study of electron transfer processes at semiconductor-electrolyte interfaces.¹ When the particle dimensions are small enough to minimize light scattering, the semiconductor suspensions have large surface-to-volume ratios that lead to enhanced optical detectability of surface effects. Prior investigations of colloidal semiconductor systems have centered on the moderate band gap, visible light absorbing materials, TiO_2 and CdS .^{2,3} The present report on ZnS represents the first time the luminescence of this wide band gap semiconductor has been studied as a colloidal dispersion. Emission properties therefore serve as a probe of interfacial electron-hole processes.

Luminescence studies of doped colloidal ZnS (as compared to CdS or TiO_2) are particularly convenient because ZnS crystals have a high emission efficiency. The emission properties of this material have frequently been used in solid-state photo- and electroluminescence studies concerned with the mechanism of semiconductor emission.⁴ The relative ease of doping ZnS with Mn^{2+} makes this an ideal luminescent probe for surface effects and photochemical processes in colloidal semiconductors. ZnS is a type II-VI semiconductor. It exists in two crystal forms: blende (cubic) and wurtzite (hexagonal), $T_{\text{trans}} = 1020$ °C. The valence band consists largely of s and p orbitals from sulfur while the conduction band is mainly due to s states of zinc.⁵ The band gap energy is 3.64 eV (340 nm), making it transparent in the visible spectral region. Induced subband gap transitions occur at energies in the visible region and therefore allow the optical detection of traps, radiative recombination centers, and surface states.

This investigation deals with studies of aqueous colloidal ZnS and the dependence of the emission intensity and spectral distribution on such factors as Mn^{2+} dopant concentration in the ZnS, the presence of dissolved oxygen or sulfide ion in solution, the presence of sulfur lattice

vacancies, photodegradation, and luminescence quenching by solution-phase reagents.

Experimental Section

Zinc sulfate (MCB), sodium sulfide (Alfa), manganese perchlorate (GFS), and poly(vinyl alcohol) of 86 000 M_R (Aldrich) were used as supplied. Deionized water was refluxed with alkaline permanganate and twice distilled before use.

Colloidal ZnS suspensions were precipitated from aqueous $\text{Zn}^{2+}/\text{Mn}^{2+}$ solutions by addition of S^{2-} in the presence of poly(vinyl alcohol) as a stabilizer. Typically, 50 mL of an aqueous solution containing 8×10^{-5} M ZnSO_4 , 4×10^{-6} M $\text{Mn}(\text{ClO}_4)_2$, and 2×10^{-6} M poly(vinyl alcohol) was stirred rapidly in a 150-mL beaker. A 1-mL aliquot of 4×10^{-3} M Na_2S was added in one portion. The resultant clear suspension had a pH of 8.3, indicating an excess of S^{2-} .

Colloidal particle dimensions were measured by photocalorimetry (PCS) using the 514.5-nm line of a Coherent Innova 90 Ar^+ ion laser. The scattered light intensity was monitored 90° to the incident laser beam with a RCA C31034 photomultiplier tube contained in a cooled Pacific Precision Instruments Model 3470 thermoelectric housing. The time dependence of the scattered light intensity was determined with a Brookhaven Instruments Corp. BI2020 real-time multibit correlator. An Intelligence System Corp. ISC Intercolor 3600 computer was used to collect and analyze the resultant data.

In experiments conducted in the absence of oxygen, the solutions were exhaustively degassed with N_2 before, during, and after the addition of Na_2S . The pH of the ZnS suspensions was adjusted to 6.8 ± 0.2 by dropwise addition of 0.01 M HNO_3 (Alfa ultrapure) along with flushing by nitrogen to remove any H_2S generated. Emission spectra were recorded with an Aminco-Bowman spectrophoto-fluorometer as a polychromator, adapted with a Princeton Applied Research Model 1215-1216 optical multichannel analyzer incorporating a Model 1254 SIT Vidicon detector. An ISA holographic grating optimized at 500 nm (147 lines/mm) was used to disperse the emission spectra; this was detected with the Vidicon. Photoluminescence spectra were generally signal averaged for 300 scans. The excitation wavelength was 300 nm. The emission spectra were uncorrected for the Vidicon tube spectral response.

Luminescence quantum yields were calculated by dividing the integrated emission intensity of the ZnS colloids by that measured from a cyclohexane solution containing

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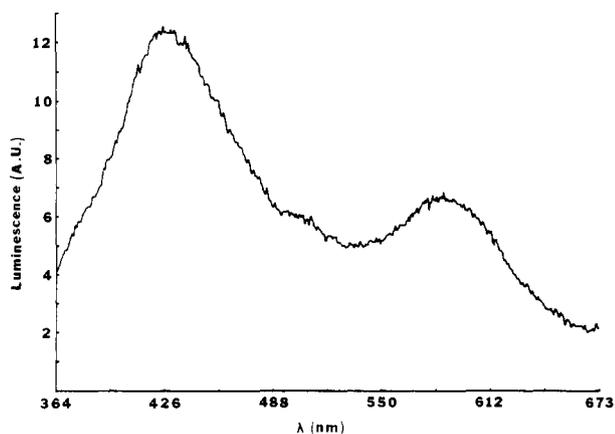


Figure 1. Photoluminescence spectra from undoped colloidal ZnS prepared under room atmosphere.

1,8-diphenyl-1,3,5,7-octatetraene (Aldrich, purified by sublimation) as an emitting standard. The absorbance of the standard solution was previously adjusted to match that of the colloid at the excitation wavelength (300 nm). The reported fluorescence quantum yield of 0.09 was used to correct the octatetraene integrated intensity.⁶

Electroanalytical studies involving oxygen concentration determinations employed a sealed Pyrex photolysis vessel containing 30 mL of stirred colloidal dispersion and a Chemtrix (Type 30) oxygen electrode. The apparatus was contained in a water bath thermostatted at 25 ± 0.5 °C and irradiated with an Oriel Model 6242 450-W xenon lamp ($\lambda > 290$ nm). The cathodic current due to oxygen reduction was measured at -0.7 V vs. Ag/AgCl reference with an IBM Model EC 225 voltammetric analyzer. A Houston Instruments Model 2000 recorder was used to display changes in the steady-state current. A Corning Model 12 research pH meter was used to measure sulfide ion concentration. Studies of the photooxidation of S²⁻ employed a Christie Electric Co. 1600-W Xe lamp ($\lambda > 290$ nm) as a light source.

Photoluminescence quenching experiments were conducted on 5% Mn²⁺-doped ZnS suspensions that were adjusted to pH 7, oxygen flushed, and irradiated until a constant emission intensity was observed. Quencher was added to the sample cuvette by syringe from stock solutions. Ammonium peroxydisulfate was recrystallized at room temperature from ethanol-water. Sodium oxalate (MCB) was used as received.

Results

Luminescence of Undoped Samples. Freshly prepared colloidal suspensions of ZnS (pH 6.7, oxygen flushed), made without intentional addition of a dopant, display weak blue (BL1) and weak orange (OL) luminescence upon ultraviolet photoexcitation at 300 nm. The emission spectrum, shown in Figure 1, is similar to that previously reported for photoluminescence of Mn²⁺-doped ZnS thin films in air.⁷ The photoexcitation spectra for both emissions agree well with the band gap photoabsorption curve, indicating that conduction band electrons and not local excitation of impurities are involved in the light-emitting mechanism. The blue emission, centered at 428 nm, lies in the spectral region associated with luminescence from self-activated centers.⁸ These centers have often

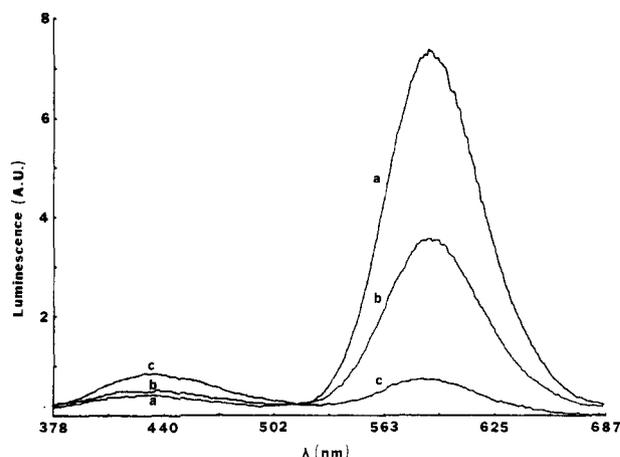


Figure 2. Photoluminescence spectra for three preparations of 5% Mn²⁺-doped colloidal ZnS: (a) excess S²⁻ added, (b) stoichiometric S²⁻ added, (c) S²⁻ titrated to pH 6.8, all three samples were oxygen flushed.

been attributed to crystal lattice vacancies. The orange emission, centered at 583 nm, arises from crystalline incorporation of trace amounts of Mn²⁺ in the crystal lattice. The Mn²⁺ was probably introduced as an impurity from either the ZnSO₄ or the distilled water (which had been distilled from a permanganate bath).

The rate of growing-in of the emission after excitation was investigated by laser flash photolysis ($\lambda = 266$ nm, $t_{\text{pulse}} = 40$ ps). These results show that the blue emission (BL1) appears immediately following photoexcitation and has a lifetime on the nanosecond time scale. Since the decay of BL1 did not follow a simple first-order rate law, a transient lifetime cannot be given. The orange Mn²⁺ luminescence is not present immediately following the excitation, but rather the intensity grows in and reaches a maximum after 22 min of excitation with a 150-W xenon lamp at 300 nm.

The relative intensities of the blue and orange emissions depend upon several factors, including the quantity and rate of sulfide ion addition during preparation of the colloid. The luminescence spectra of three identically doped and pH adjusted ZnS suspensions in Figure 2 demonstrates the effect of sample preparation. The sample that was prepared by dropwise addition of sulfide ion showed a BL1 emission which was appreciably higher than colloids generated by rapid addition of either stoichiometric or excess amounts of sulfide ion. The latter emission curves showed corresponding increases in the Mn²⁺ orange luminescence with an isosbestic point at 515 nm. The presence of the isosbestic point indicates that the OL and BL1 emissions are mechanistically related and probably share a common precursor (the conduction band electron). Since less than the stoichiometric amount of S²⁻ is needed to generate a neutral pH suspension, slow crystal growth in the presence of the zinc and manganese metal ions should give colloids which are deficient in S²⁻. Sulfur lattice vacancies have been shown important in the SAL (self-activated luminescence) band of ZnS single crystals and dry powders.⁹ The BL1 emission is the colloid analog of the SAL luminescence.

Effect of Irradiation Time. Colloidal ZnS is photochemically unstable. Upon prolonged irradiation and shaking, freshly prepared dispersions of ZnS showed a new intense blue emission (BL2, $\lambda_{\text{max}} = 418$ nm, Figure 3 curve b); this BL2 emission was about 40 times more intense than the BL1 emission shown in Figure 1. The appearance of this luminescence was accompanied by a decrease in the

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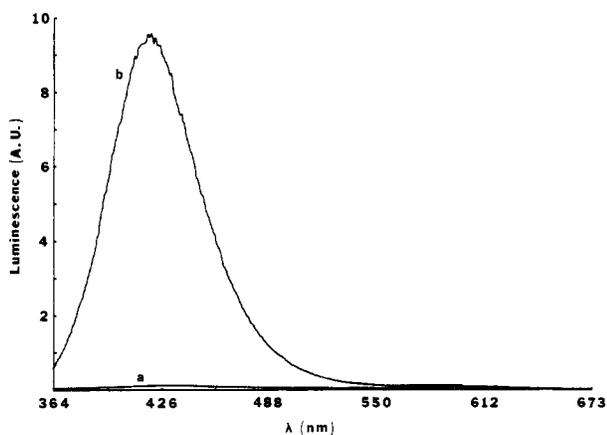
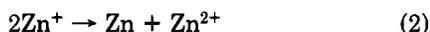


Figure 3. Photoluminescence spectra from undoped colloidal ZnS: (a) emission curve after 40 min of irradiation (same as Figure 1), (b) emission curve after shaking. The sample was prepared under room atmosphere and nitrogen flushed.

orange Mn^{2+} luminescence intensity found before agitation. Absorption spectra of photolyzed and shaken ZnS suspensions display an increase in light scattering (as indicated by a base line shift to higher absorbances) and a decrease in band gap absorption. These observations suggest that agitation of irradiated ZnS colloids leads to increases in the particle size. Furthermore, prolonged photolysis and stirring of ZnS colloids produced particles of macroscopic dimensions that settled to the bottom of the cuvette upon standing. Similar agitation of ZnS colloidal dispersions that were not irradiated did not show this aggregation. Photochemical decomposition of ZnS crystals and powders is an established phenomenon.¹⁰ Previous work has shown that the blackening of ZnS phosphors proceeds via an irreversible reduction of lattice zinc ions by conduction band electrons, while lattice sulfide ions become oxidized by holes.



Photodecomposition of dry ZnS is also enhanced by the presence of water vapor.¹¹ Because it has a high absorptivity and large surface area, colloidal ZnS might behave in a similar, but enhanced, manner. In this case, agitation of photolyzed ZnS would produce enlarged particles containing interstitial sulfur and zinc atoms. These sites, which could trap electrons and holes that radiatively recombine, are responsible for the BL2 emission. This BL2 emission is comparable to the B band luminescence reported in ZnS phosphors that contain interstitial sulfur atoms.⁹

Effect of Mn^{2+} Doping. The orange luminescence intensity ($\lambda_{\text{max}} = 583 \text{ nm}$) of colloidal ZnS was increased upon deliberate doping by Mn^{2+} (Figure 4). An increase in luminescence intensity by a factor of two was observed for colloidal dispersions aged overnight. Similar aging effects have been reported for colloidal CdS emission.^{3b} The luminescence efficiency of 5% Mn^{2+} -doped ZnS dispersions reached a maximum value of 0.08, the highest efficiency ever reported for a colloidal semiconductor dispersion. The increase in the maximum intensity of the dopant orange emission was again accompanied by a corresponding decrease in BL1 for otherwise identically prepared and pH adjusted colloids. This further illustrates the common precursor in the emission mechanism of BL1

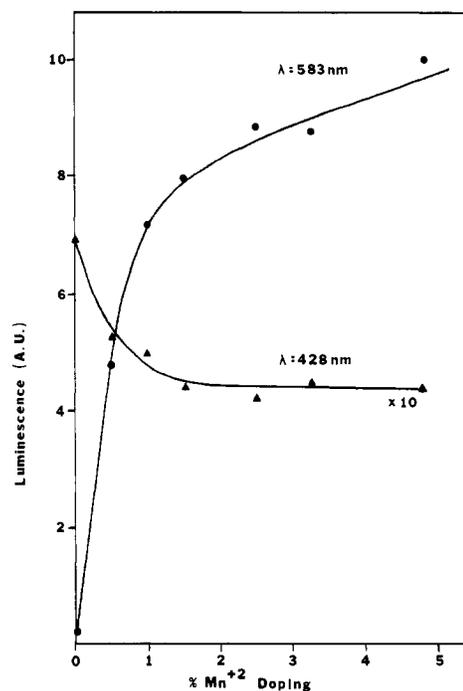


Figure 4. Dependence of OL intensity on amount of Mn^{2+} doping. The samples were prepared under room atmosphere, pH adjusted to 6.8 ± 0.2 , and flushed with nitrogen.

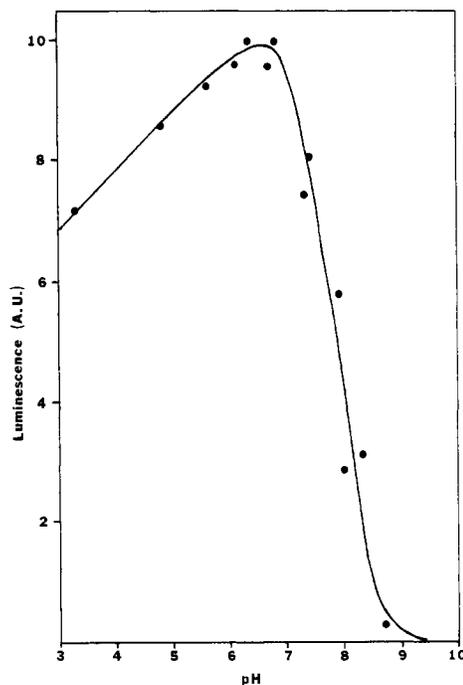


Figure 5. Dependence of OL intensity on initial pH (amount of excess sulfide present). The samples were prepared under room atmosphere and nitrogen flushed.

and OL. The appearance of the Mn^{2+} emission required the absence of excess sulfide ion and the presence of dissolved oxygen in solution.

The presence of solution phase sulfide ion in colloids prepared from stoichiometric amounts of Zn^{2+} and S^{2-} was evident by an alkaline pH of the resultant dispersion. Solution sulfide ion inhibited the growth of the orange luminescence intensity (Figure 5). Addition of Na_2S to a neutral suspension of emitting colloid (5% Mn^{2+} -doped) resulted in complete quenching of the orange emission and was accompanied by a considerable reduction in the BL1

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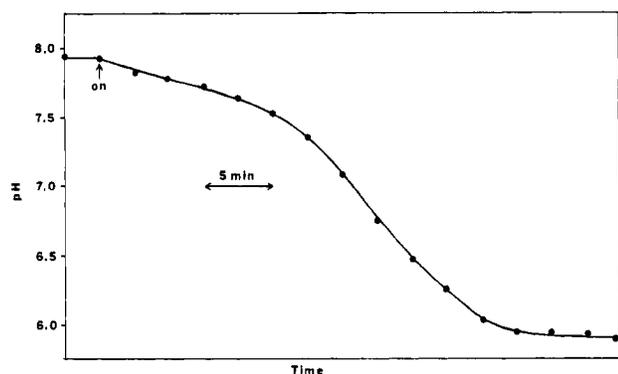


Figure 6. The colloidal ZnS photooxidation of solution sulfide ion as measured by changes in pH. The sample was prepared under room atmosphere.

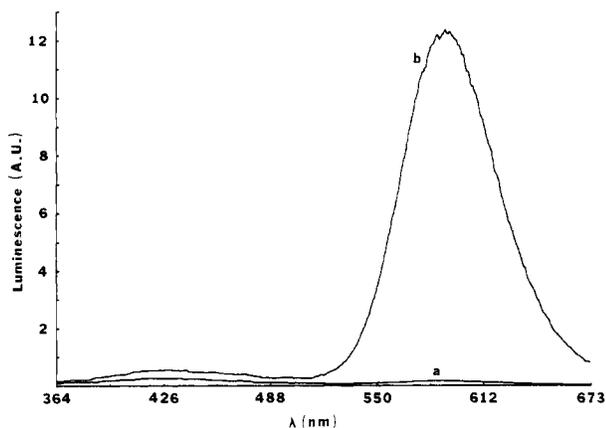
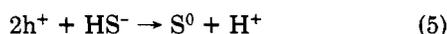
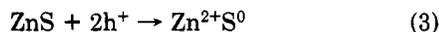


Figure 7. The effect of dissolved oxygen on the luminescence spectrum of 5% Mn²⁺-doped ZnS colloids: (a) maximum luminescence observed for a colloidal dispersion prepared under oxygen free conditions, (b) maximum luminescence observed for the same dispersion flushed with oxygen.

intensity. Increasing the pH by addition of aqueous NaOH to an emitting dispersion had no effect on the luminescence intensity. Thus, the effect of Na₂S concentration on the rate of the quenching reaction could be monitored by following the solution pH during irradiation, since sulfide ion is a base and the concentration of S²⁻ and HS⁻ vary with pH. As shown in Figure 6, the solution sulfide ion concentration (and therefore the pH of an unbuffered solution) decreased with time of irradiation. Previous studies of the photodegradation of CdS crystals have illustrated that solution-phase sulfide and selenide ions readily substitute at photooxidized lattice sites.¹² A similar photooxidation/substitution mechanism resulting in the net consumption of sulfide ion is possible for colloidal ZnS.



Effect of Dissolved Oxygen. The presence of dissolved oxygen in solution had a dramatic effect on the intensity of the Mn²⁺ luminescence (Figure 7). Colloidal suspensions of Mn²⁺-doped ZnS that were prepared under an oxygen-free atmosphere (excess HS⁻ removed by decreasing the pH to <7 by addition of nitric acid and nitrogen flushing) showed virtually no luminescence. Upon

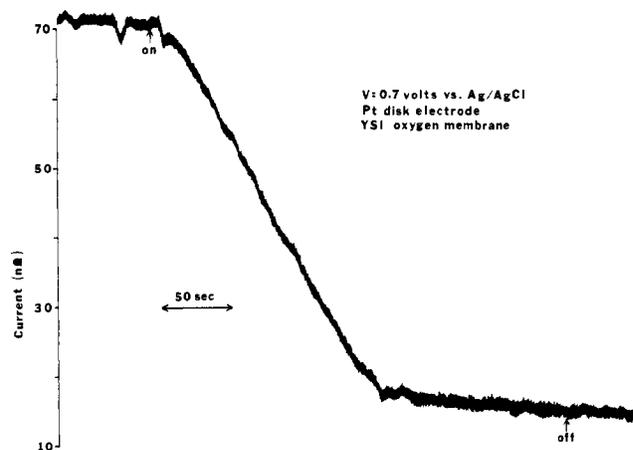


Figure 8. The change of oxygen concentration during photolysis of colloidal ZnS. The sample was prepared under room atmosphere, pH adjusted to 6.9, and flushed with nitrogen.

oxygen flushing, however, the same dispersion produced a bright orange luminescence identical with that found with colloids prepared under ambient atmospheric conditions. Electrochemical monitoring of the oxygen level revealed a decrease in the oxygen concentration with time during irradiation of the semiconductor. The effect of UV irradiation ($\lambda > 290$ nm) on oxygen concentration in solution, indicated by the cathodic current at an oxygen electrode, is given in Figure 8. The initial current represents the amount of dissolved oxygen present after sample preparation and nitrogen flushing. The decrease in current during photolysis corresponds to a decrease in oxygen concentration by about 80% (the extent of decrease depended on method of sample preparation). Addition of an acidic titanium(IV) reagent to the irradiated dispersion gave no indication of the formation of hydrogen peroxide at levels above 5×10^{-6} M.¹³ Thus photoinduced adsorption of oxygen occurs, perhaps in a reduced state, e.g.



and this adsorbed oxygen promotes the orange luminescence.

Similar oxygen effects have previously been cited for dry ZnS powders.¹⁴ These reports attribute the removal of atmospheric oxygen to photoenhanced adsorption on the ZnS surface. Chemisorption of oxygen on ZnS has been said to proceed by both thermal and radiative processes; in thermal adsorption O₂ was said to be in the form of the ion O₂⁻, while in the radiative chemisorption, the form O⁻ was proposed.¹⁵ Oxygen consumption from irradiated ZnS colloidal suspensions probably occurs by a similar photoenhanced adsorption process. The presence of oxygen or an oxide species on the surface of the colloidal semiconductors should have a profound effect on surface recombination of photogenerated electrons and holes.

Colloidal Particle Sizing by Photon Correlation Spectroscopy. The results of particle sizing experiments for 5% Mn²⁺-doped ZnS by photon correlation spectroscopy are shown in Table I. The data show essentially no variation in the effective particle diameter ($0.12 \pm 0.02 \mu\text{m}$) of colloidal dispersions stored in the dark for up to 30 h. However, the hydrodynamic equivalent spherical diameter and the *Q*(val) both decrease with time. This indicates

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TABLE I: Colloidal ZnS Particle Sizing by Photocorrelation Spectroscopy

	age of colloidal dispersion					
	<2 h	4 h	6 h	15 h	30 h	30 h ^d
diameter, ^a μm	0.25	0.21	0.17	0.15	0.16	0.59
effective diameter, ^b μm	0.12	0.10	0.13	0.10	0.14	0.43
Q(val) ^c	1.2	0.74		0.53	0.38	1.1

^a Hydrodynamic equivalent spherical diameter from the Stokes-Einstein relationship assuming a single exponential fit of the correlation function. ^b Effective diameter arising from a distribution of particle sizes and calculated from an assumed cumulant fit of the correlation function up to the second moment. ^c The relative standard deviation in the effective, spherically equivalent, hydrodynamic diameter assuming a distribution of particle sizes. ^d After irradiation with a 1600-W Xe lamp for 15 min at $\lambda > 290$ nm.

that, with "aging", the particle size distribution becomes more uniform but the effective size remains unchanged. The results were reproducible with four different colloidal dispersions. In all cases the dispersions were stored unstirred and in the dark. A sample that was stored 6 h and vigorously stirred just prior to sizing had a measured diameter that was slightly larger ($\sim 7\%$) compared to the same dispersion unstirred. This indicates that some of the increase in particle uniformity might be attributed to the settling of larger particles with time. However, comparing this result with sizing measurements of dispersions less than 2 h old show the settling effect to be only minor when considering the overall increase in particle size uniformity with time. The increase in photoemission from Mn^{2+} -doped ZnS colloids stored overnight might also be due to particle size effect.

A dramatic change in both the size distribution and effective particle diameter occurs upon irradiation of ZnS colloidal dispersion with ultraviolet light. A sample stored for 30 h in the dark and then irradiated 15 min with high-intensity light ($\lambda > 290$ nm) showed a factor of three increase in effective particle diameter (Table I). Colloidal dispersions aged 6 h and irradiated gave similar results. This is in agreement with the UV-visible absorption spectrum of the irradiated dispersions discussed above.

Quenching of 5% Mn^{2+} -Doped ZnS Photoluminescence. The photoluminescence intensity of 5% Mn^{2+} -doped ZnS was quenched upon addition of peroxydisulfate to the solution. The effect of $\text{S}_2\text{O}_8^{2-}$ on the OL and BL1 emission intensities is shown by the Stern-Volmer plots (Figure 9). Photoluminescence quenching was also observed upon addition of HS^- to emitting ZnS colloidal dispersions. At an HS^- concentration of 3×10^{-5} M 92% of the OL and 66% of the BL1 luminescence was quenched. This effect is similar to that observed for colloids prepared with excess sulfide ion (Figure 5). The photoluminescence intensity was not altered significantly upon addition of sodium oxalate, phenol, or hydroxide ion.

Discussion

Photophysical mechanisms in which charge carriers are created and annihilated in single crystal and dry powder semiconductors (especially ZnS) have been extensively reported in the physics literature. Much of this work is relevant to a description of the photodynamics of colloidal ZnS. We will try to explain the various emissions observed with colloidal ZnS based on the experimental results and previously proposed models from studies of phosphors. Relevant energy levels are shown in Figure 10.

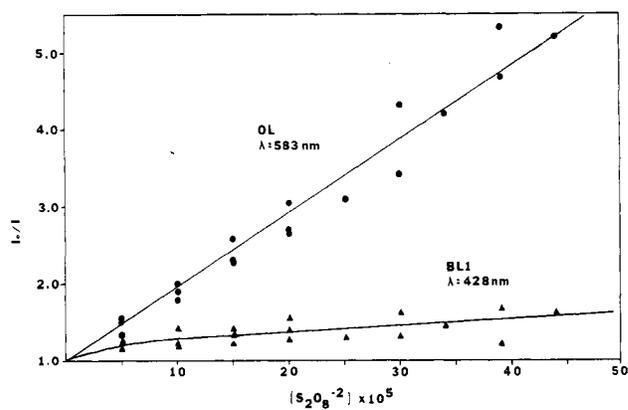


Figure 9. Stern-Volmer plot of peroxydisulfate quenching of OL and BL1 intensities. The sample was 5% Mn^{2+} -doped, prepared under atmospheric conditions, and oxygen flushed.

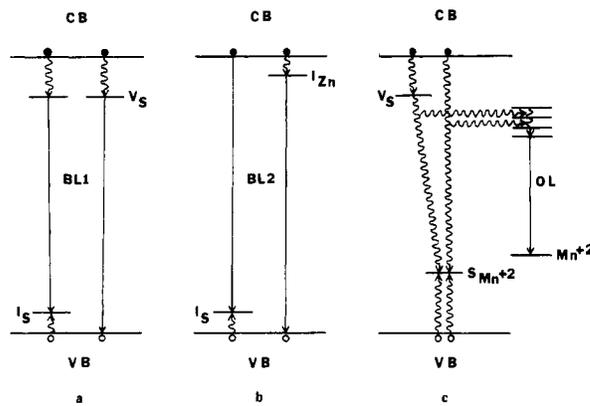


Figure 10. Luminescence mechanisms for (a) BL1, (b) BL2, and (c) OL colloidal ZnS emissions. I_S = interstitial sulfur, I_{Zn} = interstitial zinc, V_S = sulfur vacancy, and S_{Mn} = manganese substitution site.

Photoluminescence studies performed on ZnS powders have identified two of the "self-activated" emission bands as SAL and B band luminescence. Uchida has observed that SAL luminescence appears strongly in ZnS phosphors having excess zinc but disappears in phosphors having excess sulfur.⁹ He therefore suggested that the SAL center is associated with sulfur vacancies. Our experimental results with colloidal ZnS suggest a correlation between the number of sulfur vacancies and the intensity of the BL1 emission. In the preparation of ZnS suspensions the number of sulfur vacancies, and therefore the BL1 emission, depend upon the way the colloid is formed. The addition of a S^{2-} solution to a stirred Zn^{2+} solution results in colloidal dispersions which grow in a local environment rich in metal ion. When the method of preparation was inverted by adding Zn^{2+} to S^{2-} solutions, the resulting suspension showed no photoluminescence. Sulfur vacancies in ZnS generate localized donor sites; ionization of these produces a positive charge and conduction band electrons. This localized charge exerts a potential which can attract and trap electrons. This site would act as an electron donor and have an energy level just below the conduction band (Figure 10a). Emission occurs when a captured electron recombines with a hole in the valence band or in some acceptor level (Figure 10a). The high mobility of the majority charge carrier electrons favor electron trapping at donor sites. The immediate appearance and short lifetime of the BL1 band upon photoexcitation further supports the involvement of electron and not hole trapping in the BL1 emission mechanism.

The BL2 emission in ZnS colloids appeared only under conditions of prolonged ultraviolet photolysis followed by

shaking or stirring. The appearance of the BL2 emission showed no dependence on either the presence of dissolved oxygen in solution or the concentration of Mn²⁺ dopant. If the photodegradation of ZnS colloids results from oxidation of lattice sulfide by valence band holes (near the surface) and is accompanied by the reduction of lattice zinc by conduction band electrons (probably in the bulk), induced growth of the photolyzed colloidal particle could incorporate the surface adsorbed sulfur atoms and clusters.

Little is known about the energy levels of interstitial sulfur or zinc in ZnS. However, studies of the green luminescence of CdS powders suggest that interstitial cadmium and sulfur vacancies act as shallow donors (electron traps) and interstitial sulfur and cadmium vacancies can behave as deep acceptors (hole traps).¹⁶ If a similar band structure applies to colloidal ZnS, our experimental results seem to be consistent with both "Self-activated" B band luminescence in ZnS powders and green luminescence in CdS. The BL2 emission mechanism would therefore involve the trapping of either electrons or holes (Figure 10b).

The mechanism for the orange luminescence from Mn²⁺-doped ZnS colloids can be interpreted by the extension of a band model proposed by Hoshina and Kawai (Figure 10c).¹⁷ In this model Mn²⁺ acts as an isoelectronic dopant that substitutes at Zn valence sites. Ground-state ESR data of Mn²⁺-doped ZnS cubic powders show six resonance lines arising from the high-spin 3d⁵ configuration.⁵ Because the Mn²⁺-doped spectrum is the same with different electron or hole traps the emission probably occurs by transitions within the manganese d levels rather than by transitions involving other atomic sites. It has been argued that because the second ionization energy of Mn is smaller than that of Zn, the Mn isoelectronic dopant site can provide a potential to attract holes.^{17,18} Once trapped, the hole can recombine with either conduction band electrons or electrons in shallow donor sites (e.g., sulfur vacancies). The energy released upon charge annihilation promotes the Mn²⁺ center to an excited spin configuration. Radiative deactivation of the Mn²⁺ excited state results in orange luminescence (OL). The growth of the OL band at the expense of the BL1 and BL2 bands agrees with an emission mechanism involving competition for conduction band electrons and/or valence band holes.

The effect of photoinduced oxygen adsorption on the promotion of orange Mn²⁺ luminescence suggests an inverse relationship between surface-mediated charge annihilation and bulk dopant site photoluminescence. Upon ultra band gap irradiation, colloidal ZnS contains a transient population of high mobility electrons in the conduction band and low mobility holes in the valence band. In the absence of oxygen, nonradiative decay of electron-

hole pairs is efficiently mediated by active surface states. Under these conditions dopant site luminescence which involves the trapping of low mobility holes at a localized Mn²⁺ site is not observed. However, when the colloidal dispersion is flushed with oxygen (or prepared under an ambient atmosphere) and irradiated with ultra band gap light, oxygen adsorption occurs (perhaps as an oxide) and effectively blocks surface state recombination. Under these conditions the electron and hole lifetimes are sufficiently long to be trapped at a Mn²⁺ site and the resultant dopant luminescence is observed.

The peroxydisulfate quenching of the OL emission illustrates several important aspects of charge transfer quenching in ZnS colloidal dispersions. The quenching reaction involves the removal of a conduction band or trapped electron by S₂O₈²⁻. The linear Stern-Volmer plot in Figure 9 suggests that the dopant site is quenched by a diffusional process and not by preadsorption of the peroxydisulfate ion. This is further illustrated by the general insensitivity of the BL1 emission to added S₂O₈²⁻ under conditions where diffusional quenching cannot compete with very rapid radiative decay. The BL1 emission was quenched, however, by addition of HS⁻ and this supports a mechanism in which adsorbed HS⁻ reacts with a photogenerated hole. The fact that photoluminescence is quenched by an electron acceptor (S₂O₈²⁻) and remains largely unchanged in the presence of nonadsorbed electron donors (C₂O₄²⁻ and phenol) suggests that interfacial transfer of highly mobile majority charge carriers (electrons) is more facile than transfer of low mobility minority charge carriers (holes) to solution species.

While the wide band gap of ZnS prohibits the use of this material for visible light photocatalytic and photosynthetic systems, its highly luminescent nature can serve as a probe in studying interfacial charge transport.

The results on ZnS colloidal dispersions indicate that the photophysics of these semiconductor particles are very sensitive to surface effects. Photoassisted oxygen adsorption, sulfide ion luminescence quenching, photodecomposition, and light-induced particle growth all involve processes that operate at the particle-liquid interface. A characterization and understanding of the surface interactions in colloidal semiconductor dispersions is important to an overall understanding of interfacial charge transport in these systems.

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Registry No. ZnS, 1314-98-3; Mn²⁺, 16397-91-4; S₂O₈²⁻, 15092-81-6; HS⁻, 15035-72-0; C₂O₄²⁻, 338-70-5; OH⁻, 14280-30-9.

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