

Characterisation of cadmium sulphide colloids in reverse micelles

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Abstract

Colloidal microparticles of the photo-semiconductor cadmium sulphide have been prepared in reverse micelles of water/Aerosol OT/*n*-heptane. Particle sizes have been estimated by UV-visible absorbance measurements and by analytical ultracentrifugation.

Under the conditions used, reproducible and stable particles are formed at low w values, but the particle dispersion becomes unstable and sediments at higher w values (> 15) (where $w = [\text{H}_2\text{O}]/[\text{AOT}]$). Photodegradation has also been observed at w values of ≥ 10 . UV-visible measurements show that particle growth, which has been attributed to Ostwald ripening, takes place on a timescale of hours at low w values, i.e. 2.5 and 5. Ultracentrifugation data support the conclusion from absorbance measurements that growth is taking place in the system.

Photoluminescence emission spectra consist of broad, overlapping bands, the intensities decreasing with increasing w . Photoluminescence is quenched by addition of water to an already-equilibrated particle dispersion. Furthermore, the photoluminescence increases with decreasing temperature and is not dependent on oxygen content. The analysis of photoluminescence lifetimes is complicated since the decay transients are found to be multi-exponential in form. The average lifetime was found to be shorter on the high energy side of the emission and essentially independent of particle size, in agreement with previous studies on CdS colloids prepared in isopropanol glasses.

INTRODUCTION

There has been much recent interest in photo-semiconductor colloidal microparticles of materials such as TiO₂ [1], CdS [2], CdSe [3] and ZnS [4]. These systems have been examined with particular regard

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to carrying out light-mediated chemical reactions such as water cleavage to hydrogen and oxygen [5]. On photoexcitation of the micro-particles, electrons and holes are produced which can migrate to the surface of the particle and then oxidise or reduce reactants adsorbed at the surface [6]. Novel products have been obtained using dispersions of such colloids in organic solvents [7].

Much theoretical interest has also been stimulated by the observation that the band gap of semiconductor particles increases with decreasing particle size due to quantum confinement of the charge carriers. This is clearly evident in the absorbance spectra [8,9]. In addition, considerable research effort has been directed towards the use of compartmentalised media such as vesicles [10,11] and reverse micelles [12–16] for restricting particle growth such that stable particle dispersions are formed in the 0.5–5 nm size range.

This paper describes the preparation and properties of cadmium sulphide semiconductor micro-particles formed in water-in-oil (w/o) microemulsions based on the water/AOT/oil system. The addition of a stabiliser such as sodium hexametaphosphate is not required. AOT (sodium bis-*n*-ethylhexyl sulphosuccinate) is an anionic surfactant which is particularly effective in dispersing water in hydrocarbon oils such as *n*-heptane at 25°C. The resulting single-phase droplet dispersion is essentially monodisperse and thermodynamically stable [17].

MATERIALS AND METHODS

AOT was obtained from Sigma and was used without further purification. Spectrophotometric grade *n*-heptane (99%) and Na₂S·9H₂O were obtained from Aldrich. AnalaR cadmium nitrate, Cd(NO₃)₂·4H₂O, was purchased from BDH. All chemicals were used without further purification. For all experiments triply-distilled water was used.

Preparation of the colloids

Stock aqueous solutions of Na₂S and Cd(NO₃)₂ were prepared daily. Fresh stock solutions of 0.5 mol dm⁻³ AOT in *n*-heptane were prepared weekly. Microemulsions containing Cd²⁺ (or S²⁻) were made up by adding the appropriate amount of Na₂S or Cd(NO₃)₂ aqueous stock solution to a solution of 0.1 mol dm⁻³ AOT in *n*-heptane in order to give the correct *w* value where $w = [\text{H}_2\text{O}]/[\text{AOT}]$. In all cases transparent solutions were obtained on shaking.

Colloidal CdS particles were then obtained by adding the Cd²⁺-containing microemulsion to the S²⁻-containing microemulsion (in

effect HS^-) followed by shaking. This mixing process was carried out as soon as possible after obtaining clear microemulsions to minimise hydrolysis of AOT by the alkaline conditions in the S^{2-} microemulsion and to prevent sulphide oxidation to sulphur which is catalysed by the microemulsion medium [14,15]. Deoxygenation was not found to be necessary. The growth process of particles was generally complete within a few seconds. All pre-mixed microemulsions were thermostatted at the reaction temperature ($25 \pm 0.1^\circ\text{C}$).

Concentrations

The concentration of CdS is expressed as mol dm^{-3} of the total microemulsion phase volume.

Methods

UV-visible measurements were made on a HP8452A Hewlett-Packard diode-array spectrophotometer. Sedimentation coefficients were determined using an MSE Centriscan 75 analytical ultracentrifuge equipped with a UV-visible optical detection system. The detection wavelength was 275 nm. The sedimentation coefficients were determined from a plot of $\ln x$ vs time where x is the distance from the axis of rotation to the midpoint of the boundary layer. The slope of such a plot is given by $\omega^2 S$ where S (Svedbergs) is the sedimentation coefficient and ω is the rotation frequency.

Photoluminescence spectra were recorded on a Perkin-Elmer LS50 instrument, and time-resolved photoluminescence measurements were made using the single-photon counting method. An argon-ion laser was mode-locked and a DCM dye laser was synchronously pumped and frequency halved to give 340 nm radiation. The detected wavelengths were 450, 550 and 600 nm using Schott K45 (full width half-maximum (FWHM), 55 nm), K55 (FWHM, 44 nm) and K60 (FWHM, 44 nm) band-pass filters. All the experiments were conducted at 20°C . The apparatus is described in detail elsewhere [18]. Data analysis was performed using the maximum entropy method for recovery of the distribution of exponentials [19]. The software was purchased from Maximum Entropy Data Consultants Ltd. (Cambridge, UK).

RESULTS AND DISCUSSION

Spectral properties

Figure 1 shows the UV-visible absorption spectra of "freshly prepared" colloid (that is approximately 2 min after mixing the reactant-

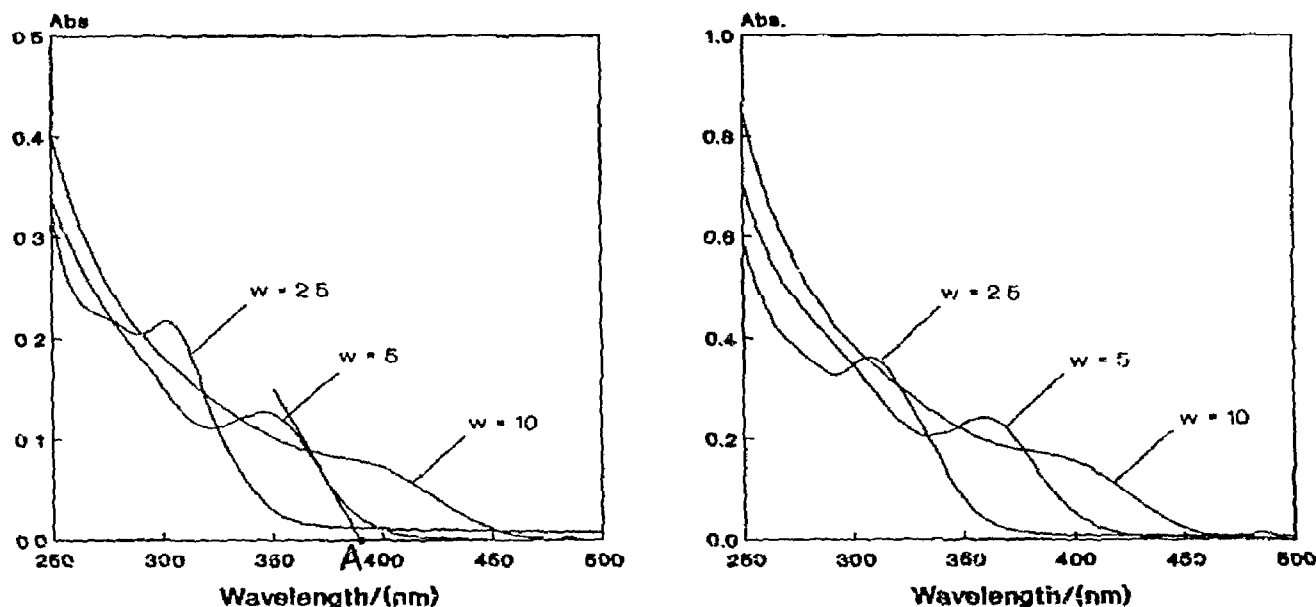


Fig. 1. UV-visible absorption spectrum of (a, left) 0.1 mmol dm^{-3} CdS (freshly prepared) in 0.1 mol dm^{-3} AOT/*n*-heptane at different w values (point A corresponds to the $\lambda_{\text{threshold}}$ value for the $w = 5$ system); (b, right) 0.2 mmol dm^{-3} CdS (freshly prepared) in 0.1 mol dm^{-3} AOT/*n*-heptane at different w values.

containing microemulsion systems) prepared using microemulsions of w values 2.5, 5 and 10. Weller et al. [8] have shown previously that there is a correlation between the wavelength corresponding to the onset of the absorption, which is approximately 520 nm in bulk CdS, and the size of the microparticles. As the particles become smaller, the onset of absorption shifts to shorter wavelengths. There is also a composition/structure correlation between w and the radius (r) of the water droplets in the parent microemulsion such that to a first approximation $r \text{ (nm)} \approx 0.18w$ [17].

It is immediately clear from Fig. 1 that as the w value is decreased, with a concomitant decrease in the droplet size in the parent microemulsion, $\lambda_{\text{threshold}}$ (the wavelength at which the extrapolation of the initial steeply rising part of the absorption spectrum crosses the wavelength axis, shown as point A for the $w = 5$ system in Fig. 1) shifts to shorter wavelengths, confirming that the size of the particles formed depends on the size of the parent microemulsion droplets. Higher w values (> 15) give rise to flocculation-sedimentation of the particles over a period of hours such that these systems are not stable. Figure 1 also shows that the size of the particles is dependent to some extent on the concentration of CdS for the $w = 2.5$ and 5 systems, i.e. larger particles are obtained with higher concentrations of CdS.

There are, however, ageing effects over a period of hours for the

$w = 2.5$ and 5 systems. These are manifested as a red shift in the absorbance onset with time (Fig. 2). This growth process which reaches equilibrium after 24 h (but without any precipitation occurring) is probably due to Ostwald ripening effects and means that particles which are freshly prepared at $w = 5$ can have a similar absorption onset to aged $w = 2.5$ particles (compare Figs 2(a) and 2(b)). However, the absorption spectrum of $w = 10$ does not change significantly with time. For w values ≥ 10 photodegradation is observed when the solutions are left in glass bottles in the laboratory without deoxygenation, as previously observed by Henglein and co-workers [20,21]. This has been attributed to photoanodic dissociation according to the equation:



This effect is manifested in the UV-visible absorption spectra by a progressive decrease in absorbance and a blue shift of the spectrum with time. The phenomenon occurs over a period of hours or days.

Variation of the organic solvent from heptane to dodecane has little effect on the appearance of the spectra of freshly prepared cadmium sulphide colloids. However, the ageing processes which we have discussed are common to all the solvents. In this connection it should be remembered that the rate constant for the exchange of material

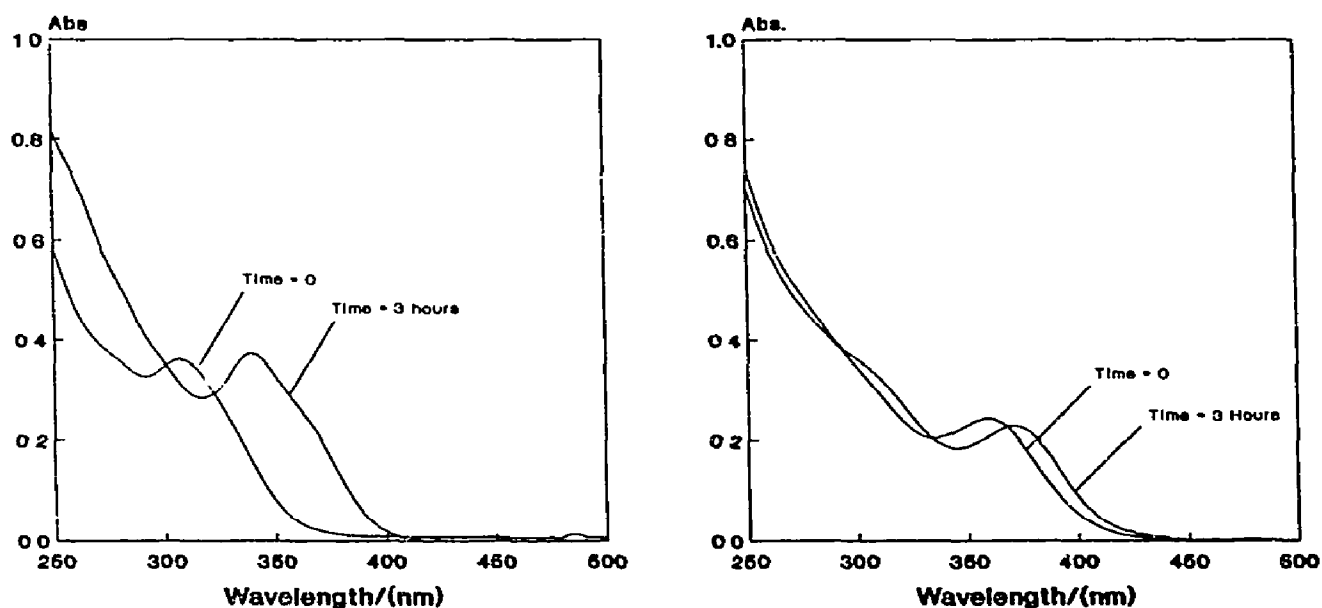


Fig. 2. Effect of ageing on the UV-visible spectrum of CdS particles prepared in (a, left) $w = 2.5$, 0.1 mol dm^{-3} AOT/*n*-heptane microemulsion, $[\text{CdS}] = 0.2 \text{ mmol dm}^{-3}$; (b, right) $w = 5$, 0.1 mol dm^{-3} AOT/*n*-heptane microemulsion, $[\text{CdS}] = 0.2 \text{ mmol dm}^{-3}$.

between droplets is dependent on variation of the solvent as reported previously [22].

Determination of sedimentation coefficient, S

These are determined for the same solutions for which the UV-visible spectra have already been discussed. Using the UV detection mode (at 275 nm) values of the sedimentation coefficient were obtained as shown in Table 1. This wavelength was used because all the particles absorb here. The values do not change significantly on dilution with the organic solvent.

The results in Table 1 show that for all the cadmium sulphide concentrations used, the value of the sedimentation coefficient increases with w value which confirms the behaviour we have previously deduced from the absorption spectra. The increase in S which is observed for the $w = 2.5$ and 5 systems on increasing the concentration of cadmium sulphide in the microemulsion at the same w value, correlates well with the small changes we observed previously in the absorption spectra (Fig. 1). On ageing of the samples, the S values for the $w = 2.5$ and 5 systems show a slight increase (Table 1), again confirming the results indicated from the absorption spectra. However, at $w = 10$, there is a very considerable increase in S with time which is not accompanied by a change in the absorption spectrum. If we infer from the spectrum that the particle size has not changed significantly, then the results can be interpreted in terms of an induced flocculation process which

TABLE 1

Experimental sedimentation coefficients, S^a , of CdS prepared in 0.1 mol dm⁻³ AOT/*n*-heptane microemulsions

[CdS] (mmol dm ⁻³)	w	$S (t = 0)$	$S (t = 3 \text{ h})$
0.1	2.5	14.7	—
0.1	5	23.3	24.1
0.1	10	61.4	168
0.2	2.5	16.3	17.3
0.2	5	24.5	26.8
0.2	10	84.6	Very large
0.4	2.5	16.7	—
0.4	5	26.7	—
0.4	10	60.1	Very large

^aIn Svedberg units.

involves attractive interactions between the particles with no real increase in size of the individual CdS particles.

Studies by Steigerwald and co-workers [3,23] on CdSe clusters prepared in reverse micellar media have provided some insight into the mechanism of flocculation on increasing the water content. An analogy was drawn between the surfactant-coated cluster and an organometallic molecule; the cluster being the central metal atom and the surfactant the ligands. The organic coat acts as a selective membrane which allows the passage of small inorganic and organic molecules to the semiconductor surface but prevents separate clusters from coagulating. Addition of water resulted in irreversible flocculation of these CdSe clusters. This was attributed to water stripping the surfactant from the particle surface, leaving open coordination sites. The particles can then touch at these sites and ultimately flocculate. The absorption spectrum does not change because the contact is only point-wise but the floc was said to be not redispersible due to strong bonds formed at the touching points. This could provide an explanation for the increase in S and the unchanged absorption spectrum for the $w = 10$ system and for the flocculation/sedimentation behaviour which is observed at larger w values as discussed previously where the flocs become so large as to sediment under gravity.

Such flocculation behaviour has also been observed for ultrafine AgBr particles prepared in water/AOT/alkane systems [24]. In this work the effect of the variation of the alkane chain length on the stability of the particles was reported. It was found that AgBr particles prepared using hexane as the continuous phase remained stable for up to several weeks. However, using higher alkanes such as tetradecane resulted in rapid flocculation. This effect was attributed to the increased interfacial fluidity and the more attractive interdroplet interactions when the alkane chain length was increased.

The sedimentograms also give some indication of the extent of polydispersity of the particles. It is clear from visual inspection of the experimental data that polydispersity increases with w . Figure 3 shows a sedimentogram of freshly prepared $w = 5$ particles and it can be seen that the particles are fairly monodisperse. This sedimentogram is typical of both the fresh and aged $w = 2.5$ and 5 colloids. This conclusion is in agreement with the work of Pileni and co-workers [16] who have reported that AOT reverse micelles produce smaller and more monodisperse particles than Triton reverse micelles or particles stabilised by hexametaphosphate (HMP) in aqueous solution. Figure 4 shows the sedimentogram of an aged $w = 10$ colloid and it can be seen that at quite low rotation speed the boundary spreads out rapidly which may be due to the polydispersity induced by floc formation.

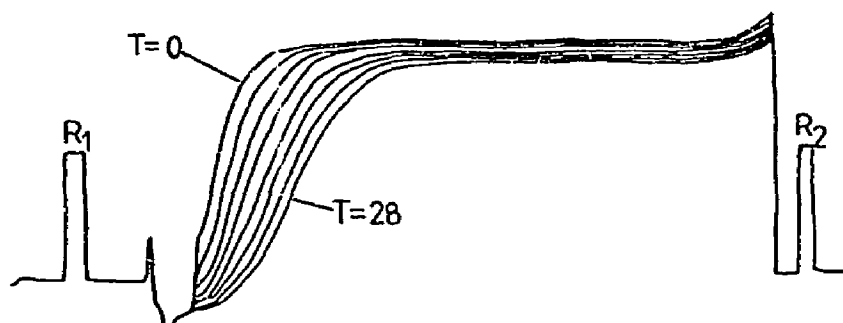


Fig. 3. Sedimentation velocity experiment carried out on freshly prepared 0.2 mmol dm^{-3} CdS in $w = 5$, 0.1 mol dm^{-3} AOT/*n*-heptane. Absorbance: full scale, 0.5; interval, 4 min; rotation speed, $25\,000 \text{ rev min}^{-1}$; scan wavelength, 275 nm; $S = 24.5$ Svedbergs.

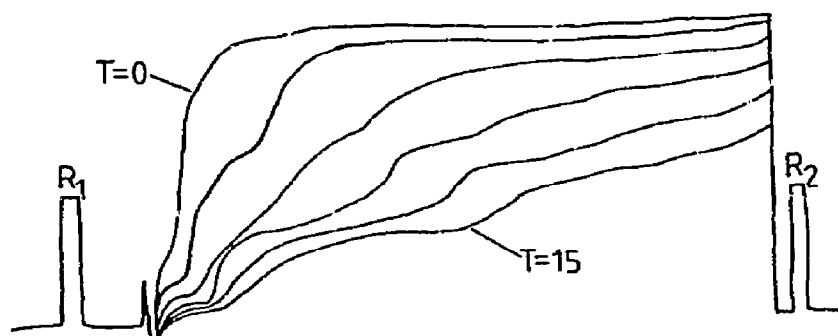


Fig. 4. Sedimentation velocity experiment carried out on aged ($t = 3 \text{ h}$) 0.4 mmol dm^{-3} CdS in $w = 10$, 0.1 mol dm^{-3} AOT/*n*-heptane. Absorbance: full scale, 1; interval, 3 min; rotation speed, $10\,000 \text{ rev min}^{-1}$; scan wavelength, 275 nm; $S > 1000$ Svedbergs.

The theoretical $\lambda_{\text{threshold}}$ vs CdS particle radius plot from the work of Weller et al. [8] allows us to make a reasonable estimate of the CdS particle radius, a' , particularly in the smaller size domain, from the absorption spectra of the particles. If we assume a model for the particle which involves a monolayer surfactant coverage of density $1.1 \cdot 10^3 \text{ kg m}^{-3}$ [25] in direct contact with a spherical cadmium sulphide particle of bulk density, with overall density ρ_p in a solvent of density ρ_s (assuming that the particle surface is not wetted by water) then we can estimate values for the sedimentation coefficient, S , based on the Stokes equation and the estimated particle radius, a' , from $\lambda_{\text{threshold}}$ where $a = a' + l$, and l is the surfactant coat thickness ($\approx 11 \text{ \AA}$):

$$S = (\rho_p - \rho_s)2a^2/9\eta \quad (2)$$

where η is the solvent viscosity. The results which are obtained using this procedure are given in Table 2 and it can be seen that for the $w = 2.5$ and 5 systems, there is rather good agreement between the calculated sedimentation coefficients obtained using the particle radius from the

TABLE 2

Estimate of sedimentation coefficient, S , of CdS particles

ω	Radius of particle (nm)	λ_{thresh}	Estimate of S^a	Experimental value of S
2.5	0.8	340 nm	13.9	14.7
5	1.1	390 nm	23.0	23.3
10	1.4	450 nm	35.4	61.4

^aIn Svedberg units.

Particle radius estimated from $\lambda_{\text{threshold}}$ of Fig. 1(a). Density of CdS, $4.8 \cdot 10^3 \text{ kg m}^{-3}$; density of AOT, $1.1 \cdot 10^3 \text{ kg m}^{-3}$; density of *n*-heptane, $0.68 \cdot 10^3 \text{ kg m}^{-3}$; viscosity of *n*-heptane, $0.409 \cdot 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$.

UV-visible absorption spectrum in conjunction with the Weller plot [8] and data obtained from our sedimentation velocity measurements.

However, the agreement is rather less good at $\omega = 10$ (Table 2). This is also the composition at which there is a rapid change in the sedimentation coefficient with time which we have associated with floc formation, so it is conceivable that the high value we have reported in Table 1 is due to flocculation having already commenced during the timescale of our sedimentation measurements (30 min).

Photoluminescence properties

The photoluminescence in CdS arises from the recombination of charge carriers or trapped charge carriers. The emission spectra consisted of broad overlapping bands. Figure 5 shows the photoluminescence emission spectra for freshly prepared (i.e. within 10 min of mixing) 0.4 mmol dm^{-3} CdS; $\omega = 2.5, 5.0$ and 10 and the concentration of AOT is 0.1 mol dm^{-3} . The excitation wavelength for all the spectra was 350 nm. It is clear that there is a red shift in the emission maximum as ω is increased and also the photoluminescence intensity decreases with increasing ω .

It has been reported that the variation of λ_{max} with $\lambda_{\text{excitation}}$ can give an indication of the polydispersity of the system [16] because if the system is polydisperse then red-shifting $\lambda_{\text{excitation}}$ will only excite the larger particles and the photoluminescence will be red-shifted. For the present work with $\omega = 2.5$ and 5.0 , λ_{max} was essentially independent of $\lambda_{\text{excitation}}$. This suggests that the system is essentially monodisperse, and this conclusion is consistent with the data obtained from the sedimentation coefficient measurements.

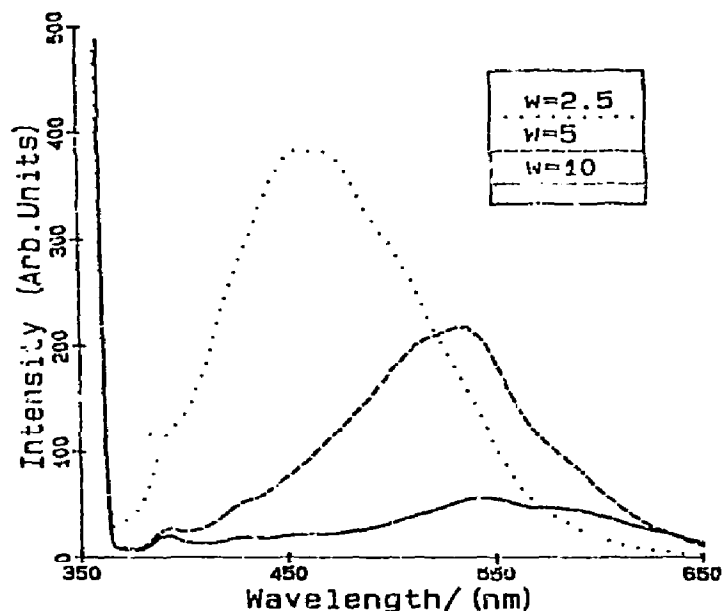


Fig. 5. Photoluminescence emission spectra of freshly prepared 0.4 mmol dm^{-3} CdS at different w values; λ_{ex} , 350 nm.

The emission spectra for a given w , as the concentration of CdS is decreased, exhibit a slight blue shift corresponding to a decreasing particle size. This concentration effect which was also evident from the absorption spectra and ultracentrifugation data has also previously been reported for CdS particles prepared on laponite powders [26].

As with the absorption spectra, there are also ageing effects over a period of a few hours for the $w = 2.5$ and 5 systems. The λ_{max} value of the photoluminescence emission shows a slight red shift with time which may again be identified with Ostwald ripening effects.

Addition of water quenches the emission as shown in Fig. 6 where water is added to an already equilibrated $w = 2.5$ particle solution. (Aliquots of water were added to an aged (i.e. already equilibrated) $w = 2.5$ solution to make the solution up to $w = 5$ and 7.5.) There is also a decrease in intensity with time, so the emission spectra in Fig. 6 were recorded immediately after addition of water. There is a further decrease of about 10% after 10 min which is accompanied by a slight red shift in the absorbance spectrum (Ostwald ripening). Further addition of water results in flocculation of the particles. It may be supposed that water quenches the emission by removing trap sites on the particle surface and destabilises the particles to Ostwald ripening and flocculation.

The photoluminescence quantum yield increases on decreasing the temperature. No change in the absorbance spectrum is observed. An interpretation can be based on thermal deactivation due to a coupling

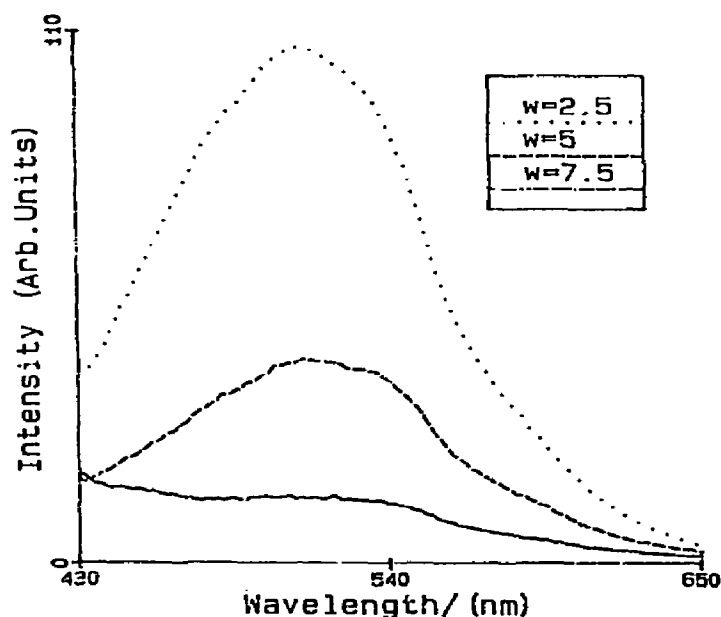


Fig. 6. Effect of addition of water on the emission of an aged $w = 2.5$ sample; [CdS], 0.2 mmol dm^{-3} ; λ_{ex} , 350 nm.

of the lattice phonons (lattice vibrations of the CdS microcrystallite) to the optical transition which can lead to a significant non-radiative electron transfer and hence to decreased emission intensity at higher temperatures [27].

Deoxygenation by the freeze-pump-thaw method produced no sizeable effect on the emission spectrum, again in agreement with the literature [28].

Photoluminescence lifetime measurements

Since the photoluminescence lifetimes were all strongly multi-exponential, it was decided to analyse the decay data using lifetime distributions composed of 200 lifetimes between 50 ps and 100 ns, equally spaced in $\log \tau$. A typical example of a decay analysis is presented in Fig. 7. The distribution pattern was not very different when the luminescence was observed at 550 or 600 nm. A distinct change was apparent on the high energy side of the emission where a clearly resolved distribution in the short lifetime regime can be observed. An average lifetime can be determined from the data which is indeed shorter at 450 nm (14.3 ns) than for the emission at 550 nm (15.7 ns). Also apparent from the results is the fact that there is a considerable contribution of luminescence lifetimes in the submicrosecond time regime. This was found to be true by analysing an experiment con-

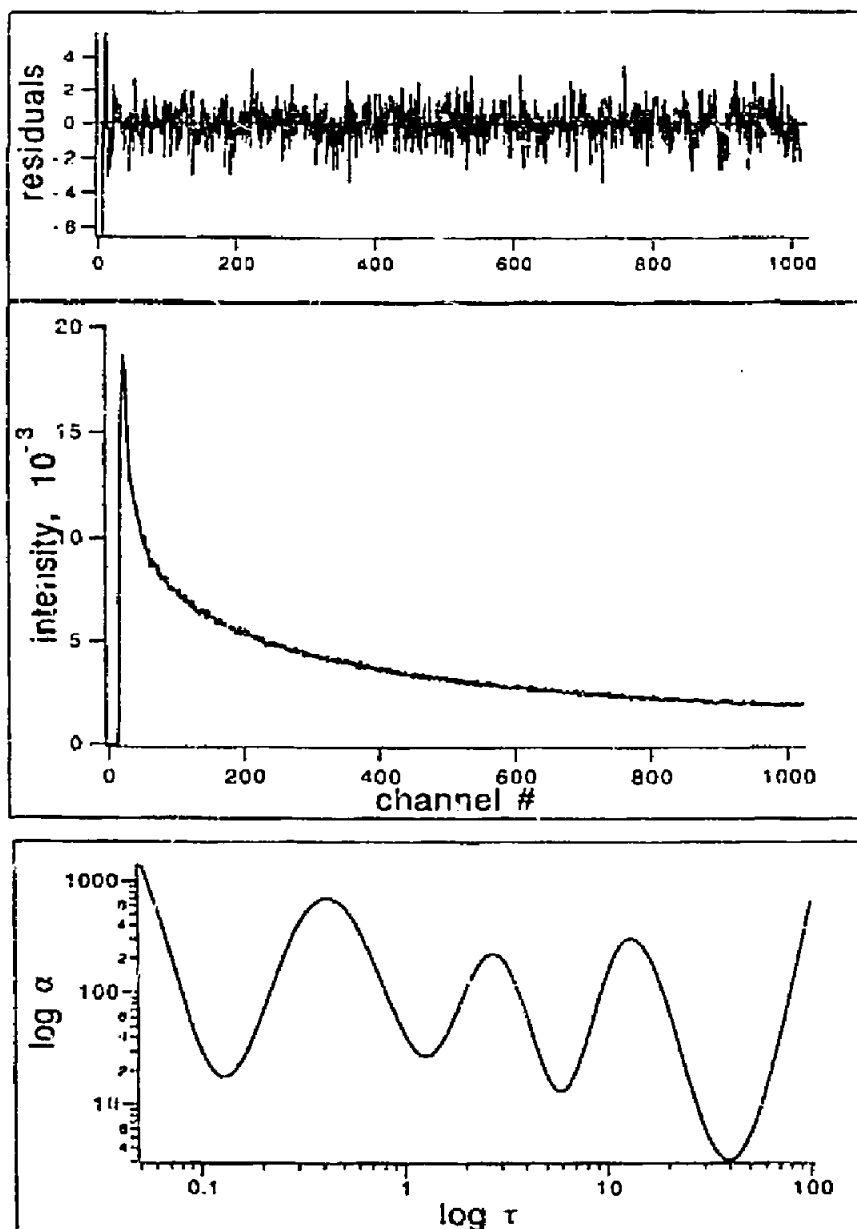


Fig. 7. Photoluminescence lifetime profile and decay analysis of CdS particles prepared in an $w = 2.5$ water/AOT/*n*-heptane microemulsion at 20°C ($\pm 0.1^\circ\text{C}$); analysis by the maximum entropy method [19]. [CdS], 0.1 mmol dm^{-3} ; λ_{ex} , 340 nm; detection wavelength, 550 nm; 0.041 ns per channel; α , amplitude factor. The microemulsion background is subtracted.

ducted at a much longer time scale (results not shown). Also in this case there was found to be a difference in lifetime distribution when the emission was observed at either 450 or 550 nm. A similar effect has been observed by Chestnoy et al. [27] and was attributed to more

closely-trapped, oppositely charged pairs emitting more quickly and at higher energy.

The transients were also very similar for equilibrated CdS particles in $w = 2.5$ and 5 systems where the particle sizes are different. A similar result was obtained by Chestnoy et al. [27] for 22 Å and 38 Å diameter CdS clusters. They observed that colloids with different absorption spectra and particle sizes had similar luminescence lifetimes, indicating that it is not the size distribution which gives rise to the emitting state distribution. They attributed the emission to a photogenerated, trapped electron tunnelling to a pre-existing trapped hole.

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