

Photophysics of Ultrafine CdS and ZnS in AOT-Heptane-Water Microemulsion

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Ultrafine CdS and ZnS in AOT-heptane-water microemulsion can be easily synthesised *in situ* by using an ultrasonic processor as homogeniser. The clusters exhibit 'the quantum size effect'. The average diameter of particles, as manifested in the photoabsorption thresholds of colloidal semiconductors, increases as the water content of reverse micelles and the concentration of *Q*-state particles increases. The emission behaviour of CdS shows a corresponding red-shift with increasing particle size and it can be effectively quenched by injecting electron/hole scavengers in the inner water pool.

Microcrystalline semiconductor particles are thermodynamically unstable with respect to bulk material and therefore require some sort of kinetic stabilisation. Organised surfactant assemblies such as vesicles¹ or reverse micelles² may be used as the incorporation media for microparticles. For small semiconductor clusters (20–60 Å in diameter), the energy levels comprising a band become more discrete and quantised (molecule-like) and the magnitude of the bandgap energy increases. This evolution of cluster properties with size has been cited as an example of 'quantum size effects'. Such effects can be observed experimentally as a shift in absorption threshold (edge) of a colloidal solution of the clusters relative to its bulk value. Theoretically, this size dependence of the semiconductor bandgap can be understood in terms of an expression proposed by Steigerwald and Brus³,

$$E(R) = E_g + \frac{h^2}{8R^2} (m_e^{-1} + m_h^{-1}) - \frac{1.8 e^2}{\epsilon R}$$

E_g is the bulk bandgap value, m_e and m_h are the effective masses of the electron and hole respectively, R is the radius of the semiconductor particle and ϵ is the bulk optical dielectric coefficient. Thus the observed shift from the bulk bandgap value is a balance between the positive kinetic energy of the system and a negative coulombic interaction. In general, the quantisation effect shows large shifts in the fundamental absorption edge and this in turn leads to enhanced redox

potentials for photoexcited electrons and holes in very small semiconductor particles (*Q*-state particles). The *Q*-state particles are expected to show extremely interesting photochemistry due to quantum confinement of the electron/hole pair upon excitation. In most of the cases intense recombination emission which is red-shifted from the absorption threshold is observed⁴. The red-shift of emission is ascribed to local trap sites arising from surface defects.

From small-angle neutron and X-ray scattering measurements, it has been shown that the radius of the disooctyl sulphosuccinate (AOT) reverse micelles is linearly dependent on W ($W = [\text{H}_2\text{O}] / [\text{AOT}]$), and so the particle size may be controlled by varying the value of W . The average particle diameter also depends on the relative amounts of M^{2+} and S^{2-} ($x = [\text{M}^{2+}] / [\text{S}^{2-}]$) (Ref. 5). In the present paper, we report quantum size effects of colloidal CdS and ZnS, stabilised in AOT-heptane-water microemulsion, at various water content with fixed concentration of the surfactant, effect of variation of surfactant concentration with fixed W (i.e. $[\text{H}_2\text{O}] / [\text{AOT}]$) and concentrations of dispersed particles.

Results and Discussion

Absorption characteristics: The CdS and ZnS suspensions are characterised by absorption spectra (Figs. 1–6). The variation of photoabsorption threshold (edge) with W (water content) for AOT-stabilised

CdS and ZnS microcrystallites has been indicated in Table 1. The absorption threshold is red-shifted with increasing W and it is due to the so-called quantum size effect. It results in a perturbation of the electron structure of the semiconductor due to a change in the

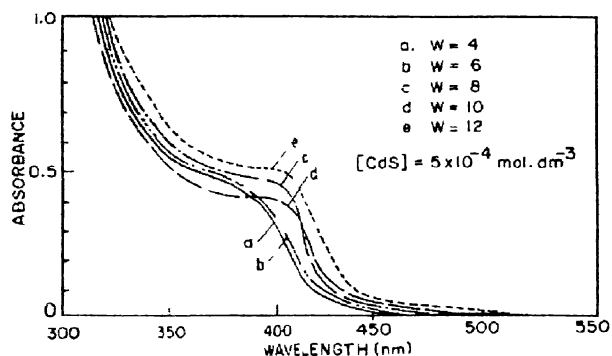


Fig. 1 Absorption spectra of CdS in 0.058 mol dm⁻³ AOT in heptane at various W values.

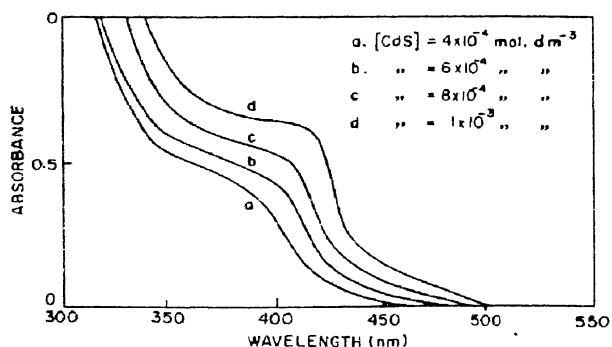


Fig. 2. Absorption spectra of CdS in 0.058 mol dm⁻³ AOT in heptane at various concentrations of CdS prepared in $W = 5$ reverse micelles

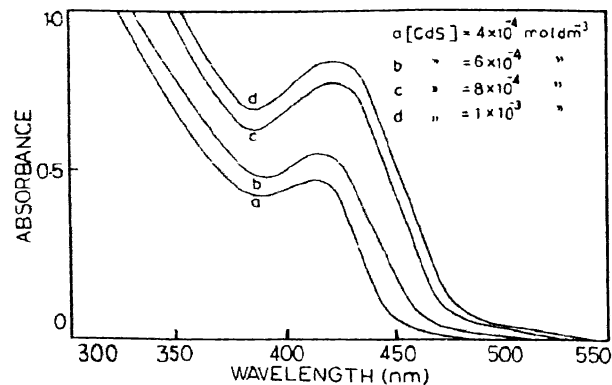


Fig. 3. Absorption spectra of CdS in 0.232 mol dm⁻³ AOT in heptane at various concentrations of CdS prepared in $W = 5$ reverse micelles.

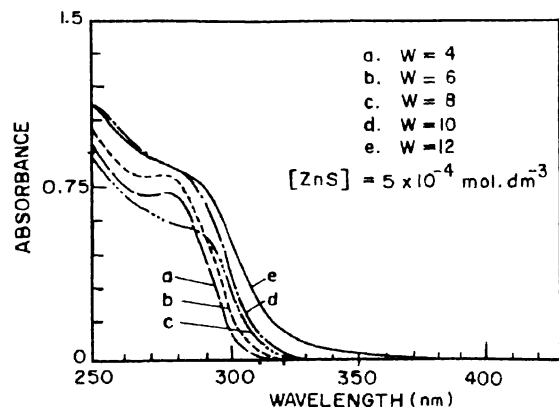


Fig. 4. Absorption spectra of ZnS in 0.058 mol dm⁻³ AOT in heptane at various W values.

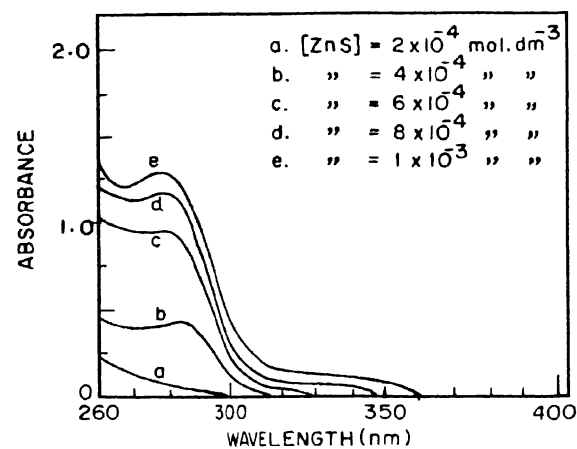


Fig. 5. Absorption spectra of ZnS in 0.058 mol dm⁻³ AOT in heptane at various concentrations of ZnS prepared in $W = 5$ reverse micelles.

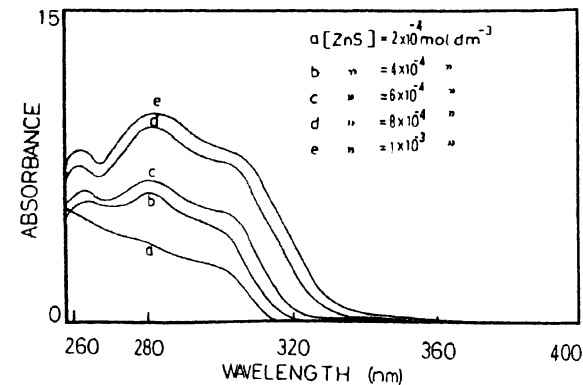


Fig. 6. Absorption spectra of ZnS in 0.232 mol dm⁻³ AOT in heptane at various concentrations of ZnS prepared in $W = 5$ reverse micelles.

TABLE 1—ABSORPTION THRESHOLDS (λ_{abs}) OF CdS AND ZnS IN AOT REVERSE MICELLES

$$\alpha = \frac{[M^{2+}]}{[S^{2-}]} = 1$$

W	[AOT] mol dm ⁻³	[Semiconductor] mol dm ⁻³	λ_{abs} for CdS nm	λ_{abs} for ZnS nm
4	0.058	5 × 10 ⁻⁴	423	302
5	0.058	2 × 10 ⁻⁴	-	297
	0.232		-	316
5	0.058	4 × 10 ⁻⁴	420	302
	0.232		450	318
5	0.058	6 × 10 ⁻⁴	430	305
	0.232		465	322
5	0.058	8 × 10 ⁻⁴	435	308
	0.232		476	329
5	0.058	1 × 10 ⁻³	440	310
	0.232		480	333
6	0.058	5 × 10 ⁻⁴	427	305
8	0.058	5 × 10 ⁻⁴	430	310
10	0.058	5 × 10 ⁻⁴	433	312
12	0.058	5 × 10 ⁻⁴	440	320

particle size. This gives a widening of the forbidden band and therefore a blue-shift of the absorption edge as the size decreases. It is possible to relate the average diameter of particles in solution to their absorption threshold. For quantised particles that have a very uniform size, one would expect to see well-defined structure in the absorption edge because of discrete levels. The absorption edge of CdS or ZnS shows a long tail at higher values of W (Figs. 1 and 4) and this arises from a broad distribution of particle sizes (polydispersion). The results presented in Table 1 also reveal that for $W = 5$, the average particle diameter of CdS or ZnS increases as concentration of dispersed particles increases at a fixed concentration of AOT. Petit *et al.*⁵ reported similar observation for CdS formed by bubbling H₂S through mixed micelles of cadmium and sodium AOT.

The results presented in Table 1 also indicate that for a given value of W , the photoabsorption thresholds of CdS and ZnS semiconductor clusters get red-shifted

as [AOT] is increased from 0.058 to 0.232 M . It implies that the radius of spherical water pool is related to [AOT], W being maintained constant at 5. Similar conclusion has been drawn by Atik and Thomas⁶ in interpreting the luminescence quenching of [Ru(bpy)₃]²⁺ by Fe(CN)₆³⁻ in the AOT reverse micelle.

Fluorescence of Q-state CdS : CdS particles in AOT-heptane-water microemulsion exhibit a broad fluorescence band with a broad peak at a wavelength longer than the edge of absorption (Figs. 7–9). The band is attributed to the removal of electrons/holes through recombination by surface charges. The energy of these traps is related to the size of the particles⁷. The fluorescence maximum is shifted to longer wavelength with the increase in pool-size of inverted micelles (evident from Fig. 7 and Table 2) and this is explained by the increase in the size of the colloids which brings about a decrease in the energy of these traps. The relative fluorescence quantum yield decreases and the fluorescence half-width increases as W increases (Table 2). The red-shifting of the emission peak with increase of CdS concentration (in $W = 5$) (Table 3) again confirms the formation of larger clusters in larger water pools. The results presented in Table 4 signify that electron scavengers like MV²⁺ and Pt and hole scavengers like HCOO⁻ and C₂O₄²⁻, on being injected in the inner water pools of reverse micelles, effectively quench the semiconductor emission by capturing electrons/holes

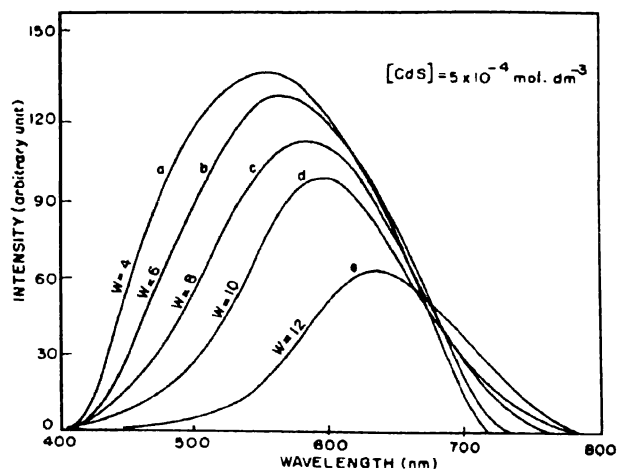


Fig. 7. Emission spectra of CdS in 0.058 mol dm⁻³ AOT in heptane at various W values.

from the conduction/valence band of the microparticles. Henglein⁸ studied the fluorescence of colloidal

CdS in aqueous medium and found similar quenching of luminescence in presence of MV²⁺ and TI⁺.

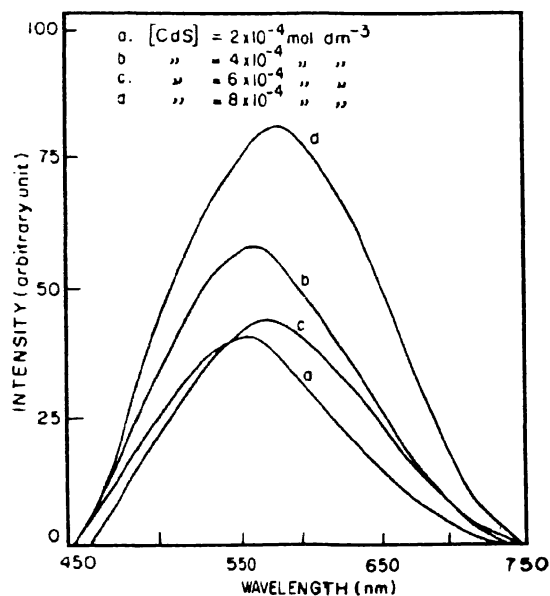


Fig. 8. Emission spectra of CdS in 0.058 mol dm⁻³ AOT in heptane at various concentrations of CdS prepared in W = 5 reverse micelles.

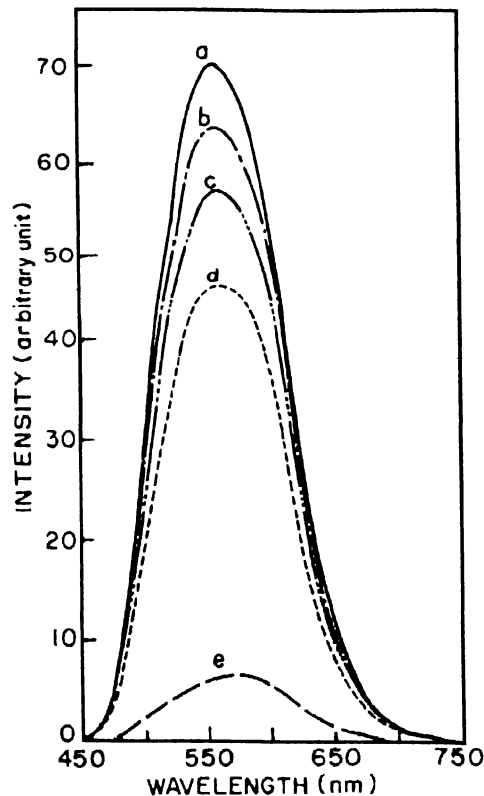


Fig. 9. Emission spectra of CdS without quencher (a); and with quenchers: (b) C₂O₄²⁻, (c) HCOO⁻, (d) MV²⁺ and (e) Pt.

TABLE 2—FLUORESCENCE OF CdS IN REVERSE MICELLES

[AOT] = 0.058 mol dm⁻³, $\nu = 1$, $\lambda_{ex} = 380$ nm, [CdS] = 5 × 10⁻⁴ mol dm⁻³

W	λ_{em}^{max} nm	ϕ_F^r	10 ⁻² ν cm ⁻¹
4	554	1	505
6	563	0.90	538
8	584	0.81	599
10	595	0.59	694
12	636	0.35	735

ϕ_F^r stands for the relative fluorescence quantum yield and ν stands for the fluorescence half-width.

TABLE 3—FLUORESCENCE OF CdS IN REVERSE MICELLES
[AOT] = 0.058 mol dm⁻³, $\nu = 1$, $\lambda_{ex} = 380$ nm, W = 5

10 ⁻⁴ [CdS] mol dm ⁻³	λ_{em}^{max} nm	ϕ_F^r	10 ⁻² ν cm ⁻¹
2	553	0.48	699
4	560	0.74	667
6	567	0.56	694
8	574	1	641

TABLE 4—QUENCHING OF CdS EMISSION BY ELECTRON AND HOLE SCAVENGERS

[AOT] = 0.058 mol dm⁻³, $\nu = 1$, $\lambda_{ex} = 380$ nm, [CdS] = 5 × 10⁻⁴ mol dm⁻³, W = 5

Scavenger	[Scavenger] mol dm ⁻³	λ_{em}^{max} nm	ϕ_F^r	10 ⁻² ν cm ⁻¹
-	-	562	1	855
COONa COONa	2 × 10 ⁻⁴	563	0.92	885
HCOONa	2 × 10 ⁻⁴	563	0.83	909
MV ²⁺	1 × 10 ⁻⁶	565	0.66	909
Pt ⁺ (1.5 wt%)	-	574	0.09	833

*Deposited photochemically on CdS surface by the reported method (Ref. 9).

Experimental

Absorption spectra were recorded on a Hitachi U-2000 spectrophotometer and emission spectra on a Hitachi F-4010 spectrofluorimeter.

The chemicals were of purest quality available and used as received.

Reverse micellar solutions were prepared to have $W = 4, 5, 6, 8, 10$ and 12 . The molar ratio of water-to-surfactant ($W = [H_2O] / [AOT]$) of $0.058 M / 0.232 M$ solution of AOT in n-heptane was prepared as a stock solution. Then calculated amount of double-distilled water was added to the heptane solution using a micropipette while the solution was sonicated vigorously with the help of an ultrasonic processor (Vibronics, Processor PI). The reverse micellar system was purged with nitrogen to remove oxygen from the solution. An aliquot of micellar solution was placed in a 50 ml beaker and purged again with nitrogen. Cluster self-assembly is somewhat dependent on the size of the reaction vessel, sonication time and the quantity of colloidal solution to be prepared. Therefore, attempts were made to keep these parameters unchanged as far as practicable.

To prepare Q -state clusters $10 \mu\text{l}$ of $\text{Cd}(\text{OAc})_2$ was added to 10 ml of the reverse micellar solution. The mixture was homogenised employing the ultrasonic processor generating intense shockwaves at the rate of 25000 per second. Then $10 \mu\text{l}$ of Na_2S (the concentration of which being the same as that of $\text{Cd}(\text{OAc})_2$) was added slowly to the mixture running the

homogeniser continuously. Finally, the colloidal solutions were allowed to stabilise for at least 30 min. To make clusters of Q -ZnS, the same procedure was carried out with a solution of $\text{Zn}(\text{OAc})_2$.

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