PHOTOCHEMISTRY OF COLLOIDAL SEMICONDUCTORS.
ONSET OF LIGHT ABSORPTION AS A FUNCTION OF SIZE
OF EXTREMELY SMALL CdS PARTICLES ☆

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The onset of light absorption of various Q-CdS samples (materials of extremely small particle size showing size quantization effects) was determined to obtain the dependence of $\lambda_{threshold}$ as a function of particle radius R. We describe the different experimental methods used for determining the size of the CdS particles. For the quantum-mechanical theory, which interprets the effect in terms of the energy levels of a spatially confined exciton, some new model calculations are reported. The previous model can be improved by introducing a finite depth for the spherical potential box representing the crystallite.

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During the last few years, a number of reports on size quantization effects in colloidal semiconductor particles have appeared [1–7]. A colloidal particle is a three-dimensional potential wall for the charge carriers which are generated upon the absorption of a photon. The quantization of the energy spectrum in the conduction band (which is almost continuous for a macrocrystal) gives rise to a blue-shift of the threshold of absorption and also of the fluorescence band with decreasing particle size. In the case of semiconductors which normally start to absorb in the infrared (band gap

< 1.5 eV) the blue-shift can be quite dramatic, i.e. several eV. In some cases, it is possible to prepare the particles in the solid state by complexing them with polyphosphate and removing the solvent by evaporation. These solid particles also fluoresce and can be redissolved with practically no changes in size. It is the purpose of the present paper to summarize the theoretical calculations and experimental findings about the dependence of the wavelength of the absorption threshold on particle size for CdS.

The first theoretical papers on quantum size effects in small CdS crystallites were published by Brus [1]. He carried out a quantum-mechanical calculation for the lowest eigenstate of the Wannier exciton consisting of an electron e^- and a valence band hole h^+, both confined to the spherical volume of the crystallite. In this model the values of the effective masses m_e and m_h in
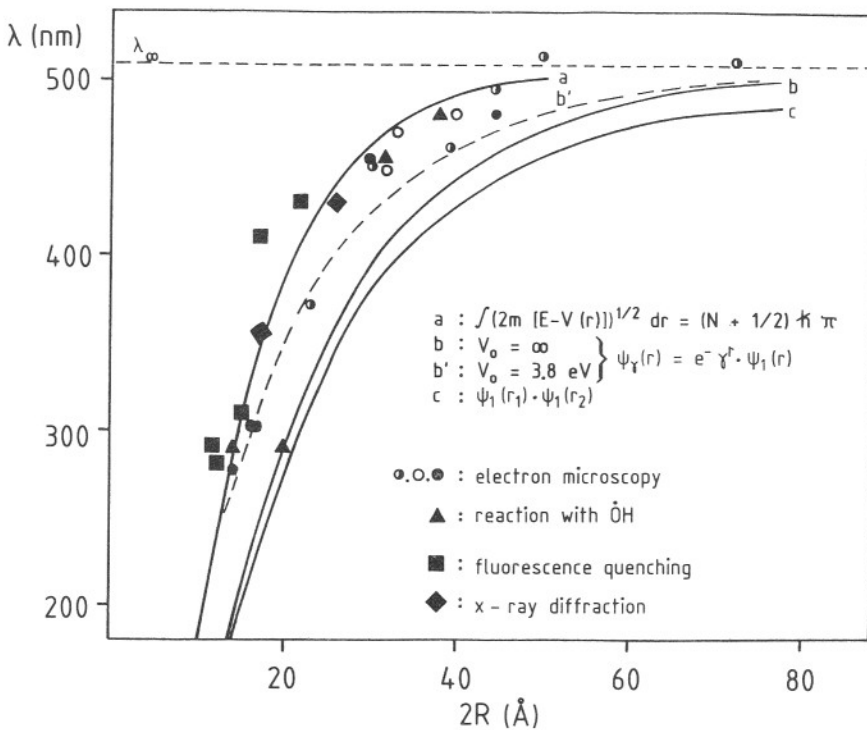

Fig. 1. Wavelength $\lambda_{\text{threshold}}$ as a function of diameter $2R$ of CdS particles; λ_∞ is the wavelength for macrocrystalline material. Points: experimental data; curves: calculated.

the bulk solid were used. Brus approximated the exciton wavefunction by one or a few configurations $\psi_i(r_e) \, \psi_j(r_h)$ of particle-in-a-box orbitals. Fig. 1 gives the wavelength of the onset of absorption as a function of the diameter, $2R$, of the crystallite. Curve c represents Brus' results.

In a somewhat rougher model, the confined exciton can be treated as one electron with the reduced mass $\mu = (1/m_e + 1/m_h)^{-1}$ which moves in the field of the walls and an h^+ fixed at the centre of the sphere. In a previous paper [2] the energy spectrum of this model system was evaluated in the semi-classical approximation. Curve a in fig. 1 gives the lowest energy level. For the same model, an accurate quantum-mechanical solution (using a wavefunction of the form $\exp(-\gamma r) \, \psi_1(r)$ [8] where the hydrogen-like factor takes account of the Coulomb attraction and $\psi_1(r)$ is the lowest particle-in-a-box orbital) yields curve b of fig. 1. Also, for the two-body model of Brus [1], we have investigated how much the energy would be lowered (i.e. curve c shifted upward) by using a better wavefunction. A

calculation with an accurate wavefunction of the Hylleraas type [9] (which explicitly contains the distance r_{eh} between e^- and h^+) shows that the threshold does not much differ from Brus' value.

All of these one- and two-body models have assumed *hard* walls for the box (potential $V_0 = \infty$ for $r > R$). The actual potential energy difference between the lower edge of the conduction band of the macrocrystal and the vacuum level amounts to $V_0 = 3.8$ eV*. This potential depth was used in the quantum-mechanical calculation of curve b'. It is seen that the energy lowering (due to the non-zero probability for the electron of staying outside the sphere) is substantial, particularly at small diameters.

The figure also contains various points which represent the experimental observations on the dependence

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* $V_0 = 3.8$ eV is in fact an upper limit as water has levels of acceptance for excess electrons at energies below the vacuum level [10]. Changes in this energy by a few 0.1 eV did not significantly change curve b'.

of the onset of absorption as a function of particle size. The size determinations were made by four methods, the first three methods applying to particles in solution, the last one to particles in the solid state:

(1) Electron microscopy. The samples were prepared by air drying a drop of the colloidal solution on a thin carbon film. Prior to this procedure the film had been exposed to a glow discharge to get a homogeneously absorbing surface. Well defined images of the small CdS particles were obtained by applying an opodization technique [11]. This results in suppression of the granulation contrast originating from the amorphous carbon film [12]. The colloidal particles were almost spherical. Larger particles exhibited lattice planes with a distance corresponding to cubic CdS. A typical size distribution of a sample containing very small particles and the corresponding absorption spectrum is shown in fig. 2. Three methods of evaluating the size distributions and spectra were chosen as illustrated in fig. 2: (a) the particle size in the maximum of the distribution curve (A) was correlated with the absorption maximum (A') (larger particles show only an absorption shoulder) (closed circles in fig. 1); (b) the particle size was extrapolated from the steeply decreasing part of the distribution curve (B), and this size was correlated with the wavelength obtained by extrapolating the steep part of the decrease in absorption at wavelengths above the first maximum (B') (open circles in fig. 1), and (c) the onset of the size distribution curve at large diameters (C) was correlated with the onset of the absorption (C') (half-closed circles in fig. 1).
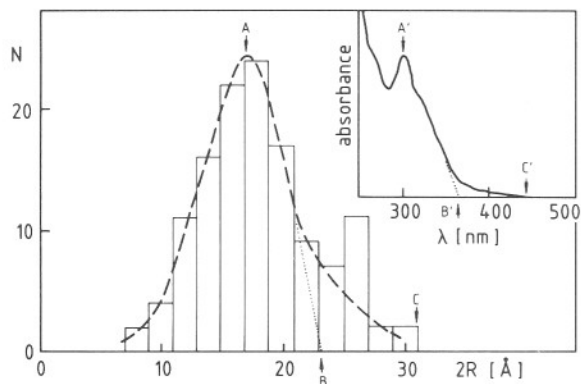

Fig. 2. Size distribution as determined by electron microscopy and absorption spectrum (inset) for a CdS sample of small particle size.

(2) Reaction with hydroxyl radicals. The rate of reaction of CdS with OH radicals is diffusion controlled. By measuring the rate of this reaction using the method of pulse radiolysis, one could derive the particle size (assuming that the particles are spherical and using a diffusion coefficient of OH of 2.0×10^{-5} cm^2 s^{-1}) [13].

(3) Fluorescence quenching with methylviologen. This compound is known to be strongly absorbed on the colloidal particles, one adsorbed molecule per particle being sufficient for quenching [14]. The concentration of the colloid particles, and from this concentration the size could therefore be derived from measurements of the intensity of fluorescence as a function of the concentration of adsorbed methylviologen.

(4) X-ray diffraction. The diffractogram showed the pattern of cubic CdS. The reflexes [111] and [002] at $2\theta = 27.0$ and $31.03°$ were observed at slightly larger angles than in the macrocrystalline material (where they are located at 26.5 and 30.7°, respectively). The line widening of the diffraction signals was used to calculate the particle diameter using Scherrer's equation: $2R = K\lambda/\beta \sin \theta$ (β is the half width of line).

Methods (2)–(4) give average diameters of the particles. They were correlated with the maxima or the shoulders in the corresponding absorption spectra.

These different methods produced consistent results as can be seen from fig. 1. Recently, Grätzel and coworkers [15] measured the absorption spectrum and size distribution of CdS particles in the range $2R = 30–45$ Å. They found a change in the band gap of roughly 0.2 eV which is in agreement with our experimental data in fig. 1.

A few remarks should still be made about the quality of the various theoretical models (curves a, b, b' and c in fig. 1). Obviously, in the hard-box model for the confined exciton (curves c and b) the increase in the band gap with decreasing crystallite size is exaggerated. The more realistic assumption of a *finite* potential energy step at the crystallite surface (curve b') improves the model considerably. The good agreement between the semi-classical curve a and the experiment must be partly fortuitous. While the semi-classical approximation gives the exact energy levels for the (hydrogen-like) free exciton, it underestimates the kinetic energy of an electron between infinitely high walls. It could be that this error is compensated by the error introduced by the infinite hard-wall assumption. Finally, we

have to be aware of the fact that the effective mass may increase with decreasing particle size. No exact method seems to exist for taking into consideration such an effect.

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