

QUANTUM STATE OF SMALL SEMICONDUCTOR CLUSTERS - "EXCITON"; RADIATION CHEMISTRY OF
"Q-STATE" PARTICLES

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ABSTRACT

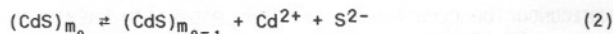
Small particles of CdS, Cd₃P₂ and ZnO have unusual optical properties. The onset of absorption is shifted to shorter wavelengths with decreasing size and a maximum is present in the absorption spectrum which is attributed to optical transitions to the "exciton" state. The fluorescence band is also blue-shifted with decreasing particle size. These effects are due to drastic changes in the electronic energy levels as a transition from semiconductor to molecular properties takes place with decreasing particle size. The effects are described by an "electron in a box" model. Pulse radiolysis was used to determine the size of the colloidal particles.

When a semiconductor is exposed to light, the photon energy of which exceeds the band gap energy, electrons in the conduction band and positive holes in the valence band are formed. Optical transitions can also occur to the exciton state which generally is located slightly below the lower edge of the conduction band. In the exciton, the electron moves around the positive hole in an orbital similar to the movement of the electron around the proton in a hydrogen atom. The Coulomb attraction between the charge carriers is weakened by the dielectric properties of the material. For example, in CdS the exciton state lies only 0.03 eV below the conduction band and the size of the exciton is about 5 nm, i.e. about 100 times larger than that of an H atom. The optical transitions to the exciton state cannot be resolved as a separate band, when the absorption spectrum of a crystal is recorded at room temperature. At liquid helium temperature, this band can be seen¹.

In very small particles, the semiconductor properties gradually are lost as a transition takes place from semiconductor to molecular material. In experiments of Brus² and ourselves³ it has been shown that the absorption coefficient decreases and the onset of absorption is blue-shifted with decreasing particle size^{3,10}. The electronic energy levels of the small particles were calculated using "electron in a box" models. Inside the colloidal particle, the screened Coulomb attraction between the charge carriers is operative. At distances $r > R$ (R = radius of colloidal particle, the positive hole being in the middle) the potential is infinite. A more detailed description of these calculations is given in refs. 3 and 4. For $R = 2.6$ nm, for example, the lowest electronic state in CdS is only slightly shifted upwards while the density of the upper states is noticeably decreased. At smaller sizes, the energy of the lowest state is drastically increased (size quantization effect).

Extremely small particles (1 - 10 nm)^{5,8} of colloidal CdS³, Cd₃P₂⁷, and ZnO⁶ were prepared in aqueous and alcoholic solutions. These particles show the size quantization effect in their absorption spectra. Macrocrystalline CdS is yellow, very small particles of CdS are colorless. Similarly, the color of Cd₃P₂ can be changed from black through various colors in the visible to white by changing the particle size. We characterize materials which show these unusual properties with the prefix "Q" before the chemical formula. The color of the fluorescence light also changes with particle size^{3,10,11}.

Under certain conditions of preparation, the absorption spectrum of Q-CdS contains several maxima (see Fig. 1). Two explanations seemed possible. One could suppose that these maxima result from transitions to various electronic states in these particles⁹. The maxima should in this case change their positions (wavelengths) when the particles grow. However, this was not observed. On the other hand, the maxima can be attributed to transitions to the exciton state in particles of different size, certain sizes ("magic agglomeration numbers") being more abundant in the size distribution than others³. Such structured size distributions can occur according to the following mechanism:



In a fast precipitation, a primary size distribution peaking at the agglomeration number m_0 is produced. The particle growth via Ostwald ripening (eqs. 2 and 3) would not lead to preferential sizes. However, when the particles grow by association (eq. 4), the original most abundant number m_0 would be preserved in the form of integer multiples. As particles of different size have different absorption, structured size distributions can be recognized in the absorption spectrum.

Pulse radiolysis was used to determine the size of the particles by making use of the diffusion controlled reaction of $\cdot\text{OH}$ radicals with the colloidal particles¹². $\cdot\text{OH}$ radicals formed in the bulk solution were used to inject positive holes into the semiconductor particles. The bimolecular rate constant, k_d , for a diffusion controlled reaction is dependent on the radius R of the particle and the diffusion coefficient D of the free radical and can be expressed by:

$$k_d = 4 \pi R D L \quad (5)$$

where $L = 6.023 \times 10^{23}$ molecules/mol and D for $\cdot\text{OH}$ radicals is $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. In pulse radiolysis experiments an overall bimolecular rate constant, k , is measured from the half-time, $\tau_{1/2}$, of the absorption change accompanying the reaction of the $\cdot\text{OH}$ radical with the colloid

$$k = \frac{\ln 2}{\tau_{1/2} c_0} \quad (6)$$

where c_0 is the overall concentration of the colloid.

The relation

$$k n = k_d \quad (7)$$

exists between k_d and k , where n is the mean agglomeration number (number of molecules CdS in one particle). If the particles are spherical

$$n = \frac{4}{3} \pi L \frac{\rho}{M} R^3 \quad (8)$$

where ρ and M are the density and molecular weight of the colloidal material.

From eqs. 5, 7, and 8 the diameter, d , of the colloidal particles can be calculated^{13,14}.

$$d = 2 \times \left(\frac{3 \times 10^{-3} M D}{k \rho} \right)^{1/3} \quad (9)$$

The diameters thus determined agree fairly well with the mean diameters determined from electron-microscopic measurements.

Further, the absorption spectrum of the product of the OH reaction was observed. It has a broad absorption band in the visible or near infrared and is thought to be a positive hole trapped at the surface. Anodic corrosion of semiconductors is a great problem in electrochemistry¹⁵. Pulse radiolysis may help to elucidate the mechanism of corrosion. The absorption of the trapped hole is thought to be due to the transfer of an electron from S^{2-} into an unoccupied electronic level of the semiconductor particle giving an absorption band at longer wavelengths in the visible. With decreasing particle size, the absorption band of the hole is blue-shifted as the electronic levels in the particle are shifted to higher energies (see Fig. 2). Oxygen was found to react with the trapped positive holes in sulfide and phosphide semiconductor particles.

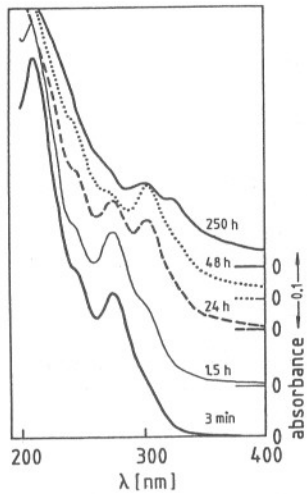


Fig. 1

Absorption spectrum of "Q"-CdS at various time periods after preparation. 2×10^{-4} M CdS and 2×10^{-4} M $\text{Na}_6(\text{PO}_3)_6$. The spectra drifted in the vertical direction, zero line indicated on the right ordinate axis.

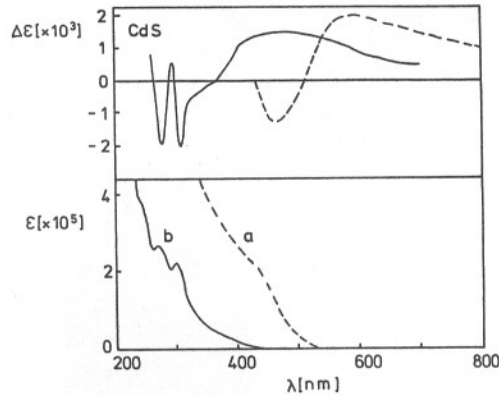


Fig. 2

Absorption spectra of CdS colloids of different particle sizes (lower part) and the change in specific absorbance $\Delta\epsilon$ at 300 μs after pulse (upper part). Mean agglomeration number: a = 266 (d = 3,2 nm) b = 94 (d = 2,0 nm)

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