

STRUCTURE AND ELECTRONIC STATES OF QUANTUM SEMICONDUCTOR CRYSTALLITES

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Introduction

Semiconductor crystallites in the 1-10 nm diameter range typically show a three dimensional quantum size effect in their electronic structure, and are referred to as quantum dots or quantum crystallites (hereafter, QCs). There has been a growing research interest in QCs as methods have been found to synthesize them, and to chemically control their surfaces to impart specific solubility properties. Crystallites with organic groups chemically bound to surface semiconductor atoms are referred to as "capped". Attempts to make concentric, layered QCs of two different semiconductors, analogous to semiconductor thin layer "quantum well" superlattices, have been reported. These QC materials can be obtained as pure, free flowing powders. In this short manuscript we review some aspects of our own work on QCs, and point out major unsolved problems. More extensive reviews of the general literature are available (1,2).

Structural Characterization

A 3.5 nm diameter capped crystallite has some 800 semiconductor atoms, about one third of which are on the surface and may be bonded to organic groups. Typical synthetic methods produce QCs with diameter standard deviations of 10-15%, and thus samples invariably have inhomogeneous distributions of sizes, shapes, and presumably surface structures.

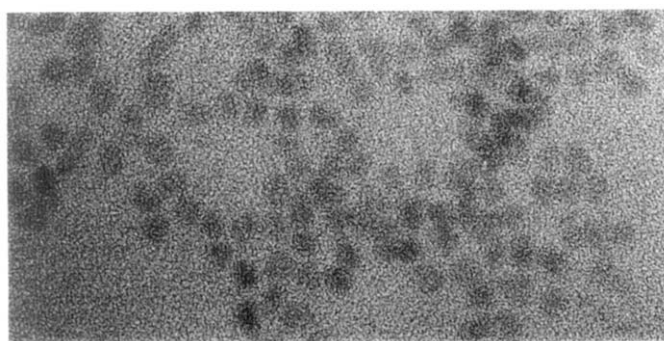


Fig. 1 TEM micrograph of 3.2 nm diameter CdSe crystallites.

These distributions apparently prevent crystallization of the QCs into single crystals. In the absence of single crystals, x-ray powder scattering and transmission electron microscopy (TEM) offer the most generally useful structural data. Fig. 1 shows a TEM of 3.2 nm diameter wurtzite CdSe crystallites. Individual sizes and shapes can be directly measured. X-ray powder patterns reveal average long range internal structure, and at this level

show the crystallites to be excised fragments of the bulk lattice. For example, Fig. 2 shows the powder patterns of two different syntheses of CdSe crystallites, and theoretical fits from computer modelling of the Debye scattering equation (3). The Fig. 1 crystallites in (b) are nearly wurtzite in structure, without change in bond length from the bulk. The finite widths of the peaks correspond to the measured particle diameter in TEM. On average, these particles have one stacking fault per particle along the C axis, analogous to a twin. The (a) particles are made in a different synthesis. Their structure is best fit by assuming random growth along the C axis.

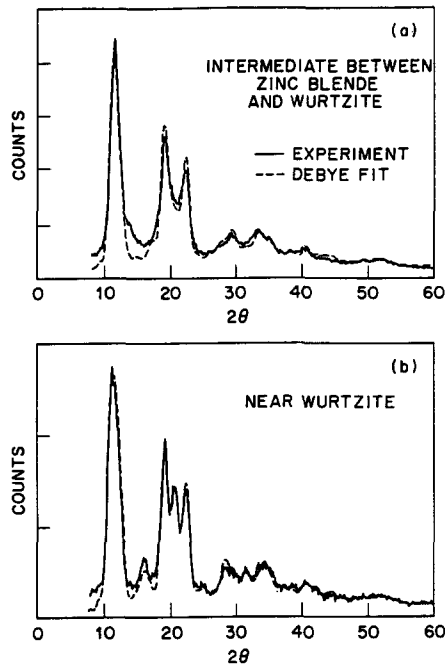


Fig. 2 CdSe QC x-ray powder patterns from ref. 3.

In both cases, we find that the computer fits are almost insensitive to assumed surface reconstruction, and/or systematic changes in bond length that conserve the average bond length within one QC. These changes typically produce small peaks that merge into the diffuse background in room temperature scattering.

While x-ray scattering measures average long range structure, EXAFS studies on Cd or Se nuclei measure average local structure. For example, Se EXAFS on (a) type QCs at low temperature shows an average coordination number of 3.64, and a "static strain," essentially a measure of the bond length dispersion across the particle, of 0.00005 \AA^2 (4). The coordination number is low as surface Se atoms are not four-fold coordinated. Yet, the measured bond length dispersion across the particle is very small, showing that surface reconstruction does not significantly change bond lengths. This result is in qualitative agreement with theoretical studies that predict bond rotation for surface atoms.

Structural characterization of putative layered, concentric QCs, such as a possible 1.2 nm thick CdSe outer layer grown on a 2 nm diameter ZnS seed, presents a serious challenge to current characterization methodology. For example, Fig. 3a shows the calculated Debye equation x-ray powder pattern for such particles where it is assumed that the CdSe layer is coherent with itself around the particle, but not coherent with the internal ZnS seed (5).

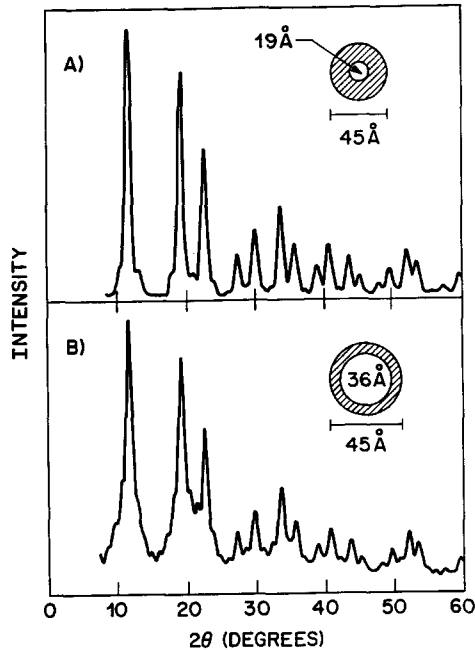


Fig. 3 Calculated concentric QC powder patterns from ref. 5.

The scattering by the small ZnS seed is very weak and broad compared with that of the outer layer. The scattering by the outer layer is essentially unchanged from that of a homogeneous CdSe QC of the same diameter. The "missing" core only causes weak lines in the diffuse background, in analogy to the surface reconstruction modelling previously described. Figure 3b shows this effect for a 3.6 nm core. An attempt to synthesize such particles, using organometallic methods in inverse micelle solutions, has been reported (5). The x-ray powder patterns observed were indistinguishable from those of pure CdSe QCs prepared by the same methods. Further development in structural methodology is necessary.

Electronic Structure and Excited State Photophysics

The simplest level of theory models the evolution of molecular orbitals in small clusters, to Bloch continuous bands in the bulk semiconductor. This is a simple exercise in the three dimensional quantum size effect ("electron and hole confined within a sphere"), if the QC exhibits the same unit cell as the bulk, as is experimentally the case in the CdSe crystallites. The Coulomb attraction between electron and hole can be also considered: it introduces an internal correlation into the joint electron-hole wavefunction as size increases. However for 3.2 nm CdSe particles the primary effect is simply the collapse of continuous bands into discrete molecular orbitals due to the quantum size effect, as illustrated in Fig. 4. In essence, the theory predicts that the QC should have a molecular-type electronic spectrum, with a number of discrete excited electronic states (6).

The molecular orbitals are characterized by radial and angular momentum quantum numbers N and L . The HOMO and LUMO are of $1S$ symmetry, with nodes on the QC surface. Allowed transitions conserve the principal quantum numbers, if the anisotropic parts of the hole effective mass tensor are not included. When they are included, transitions changing N become modestly allowed.

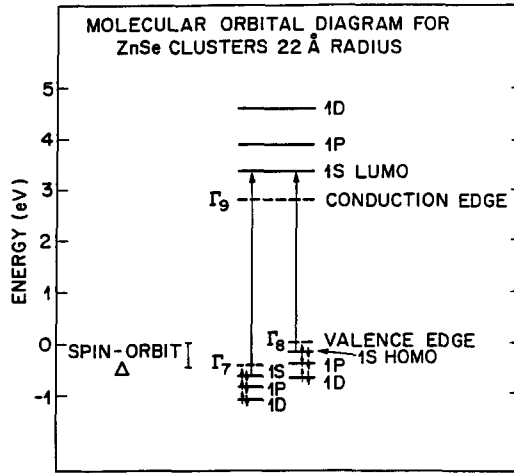


Fig. 4 Molecular Orbital Diagram for 4.5 nm ZnSe QC from ref. 6.

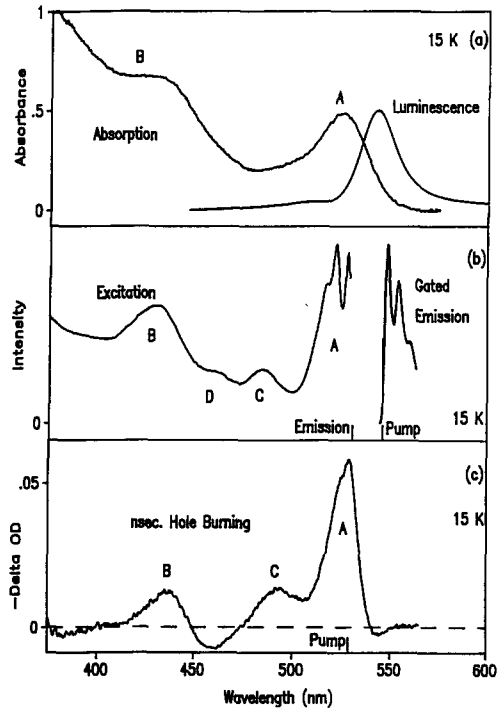


Fig. 5 Spectroscopic data for CdSe QCs from ref. 7.

Fig. 5 shows the results of optical photoluminescence and hole-burning experiments on a low temperature organic glass containing the 3.2 nm wurtzite CdSe crystallites (7). The absorption spectrum shows two partially resolved excited states A and B. A is the lowest (1S1S) excited state, shifted to higher energy than the bulk band gap at 682 nm. This state shows a mirror image, featureless luminescence. The luminescence is inhomogeneously broadened by the size and shape distribution, with smaller crystallites emitting on the higher energy side and larger ones on the lower energy side. The photoluminescence excitation spectrum of a narrow band on the high energy side shows newly resolved excited states C and D, and LO phonon structure in the lowest state A.

Correspondingly, luminescence excited on the low energy edge comes from only the largest crystallites in the distribution and shows well resolved phonon structure. Nanosecond and picosecond hole-burning spectra in Fig. 5C also show improved resolution, but not to the extent seen in the photoluminescence data. This occurs because the 1S1S absorption spectrum has an intrinsic broadening of about 130 cm^{-1} , far larger than that of the crystallite luminescence. It is believed that this is a lifetime broadening: the excited state localizes on the surface within 100-200 fs. The luminescence, occurring on a ns and longer time scale at 15K, comes from this surface localized state lying about 100 cm^{-1} below the 1S1S state. It has been conjectured that the hole localizes on a surface Se atom bonded to only three Cd atoms. A major present challenge is understanding if this is true, and furthermore how to control the localization process.

In Fig. 5b, the LO Franck-Condon structure on the lowest 1S1S state is actually weaker than that observed for the lowest exciton in bulk CdSe. This effect was originally discovered in an earlier resonance Raman study on capped CdSe crystallites (8). It is thought to occur because the Frohlich vibronic coupling weakens in small crystallites as both electron and hole tend to occupy the same 1S spatial orbital.

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