

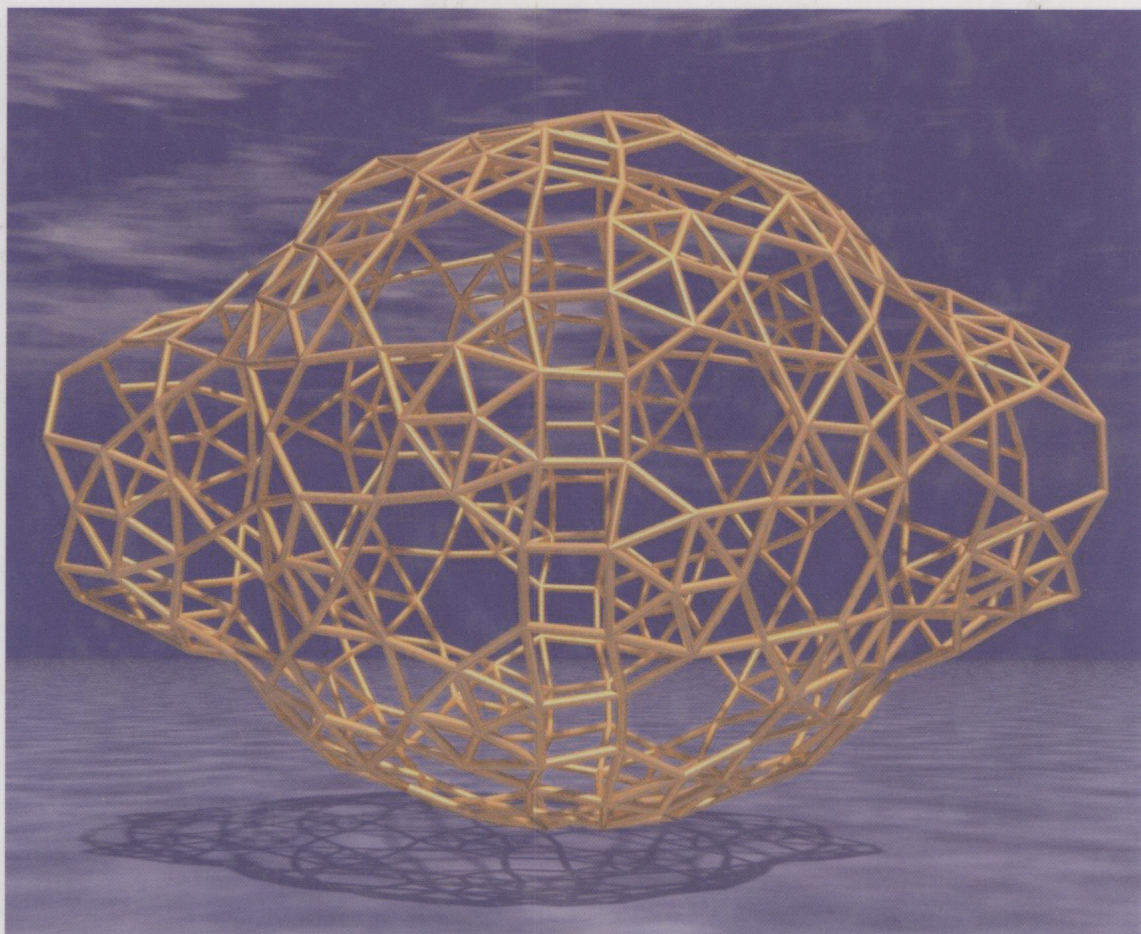
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C. N. R. Rao, A. Müller, A. K. Cheetham

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The Chemistry of Nanomaterials

Synthesis, Properties and Applications

Vol. 2

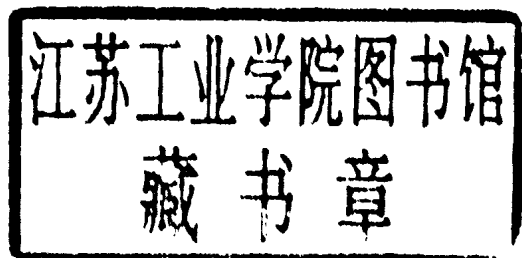


C. N. R. Rao, A. Müller, A. K. Cheetham (Eds.)

The Chemistry of Nanomaterials

Synthesis, Properties and Applications in 2 Volumes

Volume 2



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11

Electronic Structure and Spectroscopy of Semiconductor Nanocrystals

S. Sapra and D. D. Sarma

11.1

Introduction

There has been a tremendous increase in research in the field of nanocrystals during the past decade [1–7]. Although research on nanocrystals started in the early eighties, the spectacular level of activity was witnessed only in the nineties with the emergence of improved techniques for the synthesis of high quality nanocrystals and better instruments to characterize them. Also, the growing demand from the electronics industry to reduce the size of the integrated circuit chips gave the field of nanotechnology a tremendous boost.

Solid materials can be categorized as metals or semiconductors, depending on their ability to conduct electrical charge. On a microscopic level, this implies that the metal has overlapping valence and conduction bands, allowing the electrons to move freely, and thus giving rise to charge conduction. Semiconductors have fully filled valence bands and the entirely empty conduction band is separated from the valence band by a forbidden range of energies. Thus, conduction in such materials requires a finite energy to promote the electrons from the valence to the conduction band. While metals do not show much change in their electronic properties down to very low sizes, but semiconductors exhibit interesting variations in their properties at sizes of about 10 nm (100 Å) and below. One thing that is most noticeable in the case of semiconductors is the variation of the band gap with a decrease in the size of the nanocrystals below the Bohr exciton radius, a_B , of the semiconductor. For example, the band gap of CdS, a II–VI semiconductor, can be made to vary more or less continuously from the bulk value of 2.4 eV up to about 4.0 eV observed for a 15 Å nanocrystal by merely tuning the size of the CdS nanocrystals [8]. Other properties such as the melting point also depend strongly on size. For example, while the melting point of bulk CdS is $\sim 1600^\circ\text{C}$, 2.5 nm CdS crystallites melt at a temperature as low as $\sim 400^\circ\text{C}$ [9]. Optical properties such as fluorescence emission are also critically dependent on the size of the nanocrystals. For example, it has been shown that various sized CdSe nanocrystals can fluoresce throughout the visible range of the electromagnetic spectrum [10] with suitable control of the particle size.

The structure of the nanocrystalline materials plays an important role in determining electronic properties. The same material can crystallize in different structures upon size reduction, depending on the reaction conditions. Such structural transformations are discussed in Section 11.2.

As already pointed out, the most direct consequence of a reduction in the nanocrystallite size on the electronic structure of semiconducting materials is a pronounced increase in the band gap due to the quantum confinement effect. While there are several ways to quantitatively understand this phenomenon from a theoretical standpoint, the experimental determination of the band gap variation as a function of size is most directly performed by ultraviolet–visible absorption spectroscopy, with the experimental absorption threshold corresponding to the direct band gap in the material. As the band gap shifts to higher energy, the blue-shift in the absorption edge signals the formation of progressively smaller sized nanocrystals. Therefore, UV–Vis absorption spectroscopy has played an immensely important role in the study of these systems and we discuss the essential aspects in Section 11.3.

The UV–Vis absorption process generates an excited state of the system by generating an electron in the conduction band and a hole in the valence band; this state most often de-excites via a radiative process, giving rise to fluorescence. The emission characteristics depend on various aspects of the electronic structure of the nanocrystallites. Thus, the tuning of the fluorescence wavelength in nanocrystals can be achieved by a variety of methods as discussed in Section 11.4.

A lot of theoretical work has been done in order to explain the size dependent properties of semiconducting nanocrystals. These methods are primarily based on the effective mass approximation, pseudopotential approaches or the tight binding scheme. Each of these methods has certain advantages and disadvantages. We shall explore these methods in some detail in Section 11.5.

Photoemission experiments that probe the electronic structure of the nanocrystals are indispensable if one wishes to gain insight into the electronic structure–property relationship. Though very few studies have been carried out on semiconducting nanocrystalline systems to date, techniques such as photoemission and X-ray absorption spectroscopies are of immense value in probing the electronic structure and also in verifying various theories proposed for the nanocrystals. In Section 11.6 we discuss these spectroscopic studies.

11.2

Structural Transformations

Solids are known to exist in different structural phases depending on the temperature, pressure and other ambient conditions. Semiconductors, especially the group IV, II–VI and III–V that are more covalent than other compounds, prefer tetrahedral coordination around the ions, giving rise to phases such as the zinc blende or the hexagonal phase. Ionic solids are stable in higher symmetry octahe-

dral phases such as the rock salt structure. It is easy to imagine the conversion from tetrahedral coordination to octahedral coordination. Applying pressure to the tetrahedron it can be flattened out to give a square planar structure. Two atoms from the top and bottom can come closer to form an octahedron. Although C and Si, which are highly covalent, would be unstable in octahedral coordination and prefer tetrahedral coordination owing to their sp^3 hybridized orbitals, II–VI and III–V semiconductors, that have some degree of ionicity, can be transformed to the octahedrally coordinated structure by application of pressure. It has been found in the case of CdSe nanocrystallites that the wurtzite nanocrystals are transformed to the rock salt phase by application of 2–9 GPa pressure [2]. Phase transformations from the stable wurtzite phase to the zinc blende structure have been observed in the case of CdS nanocrystals as a function of the nanocrystal size [11]. Figure 11.1 shows the wide angle X-ray diffraction patterns for CdS bulk, and 4.5 nm and 2.2 nm nanocrystals of CdS. The bulk and the larger 4.5 nm nanocrystals exhibit the characteristic wurtzite phase structures, though the pattern for the nanocrystals is broader than that of the bulk. This broadening is exploited to measure the particle size from the X-ray diffraction pattern using the Scherrer formula for spherical particles,

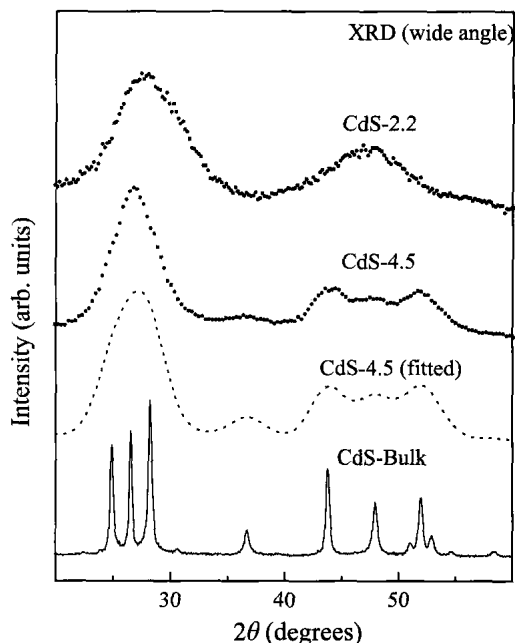


Fig. 11.1. X-ray diffraction patterns for bulk CdS, 4.5 nm and 2.2 nm CdS nanocrystals. Also shown is the broadened bulk pattern for spherical CdS nanocrystals of 4.5 nm diameter. Note the change in the structure for the 2.2 nm nanocrystals as seen between 2θ equal to 45° – 55° . Adapted from [11, 99].