

Nanoclusters, Nanoparticles and Size Quantization Effects. (Approach to Nanoparticles and Nanostructures.)

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During the past two decades, “small-particle” research has become quite popular in various fields of physics and chemistry. By “small particles” are meant clusters of atoms or molecules of metals, semiconductors and others materials, ranging in size from < 1 nm to almost 10 nm or having agglomeration numbers from <10 up to a few hundred, i.e., species representing the neglected dimension between single atoms or molecules and bulk materials.

Presentation intends to show some findings, ideas and opinions obtained during 14 years in the field of nanoparticles and nanostructures (in the EUREKA framework) and to attract peoples attention to these phenomena based on such results.

Presentation is aimed at:

- explanation of the nanoparticles construction and creation
- behaviour and physical properties of nanoparticles
- demonstration of practical usage of nanoparticles (luminescence of Si in org. solution)

Presentation will not deal with theoretical calculations and will omit complicated derivations which can be found in our and other related publications and articles.

Presently there is a great interest in applications of nanotechnology.

Following general idea prevails:

Nanotechnology is a branch of science dealing with very small material objects with dimensions of the order of nanometers (several units, tenths, up to several hundreds) exhibiting individual character and being unique by its construction and its functioning (e.g. biological engine of circular or pyramidal geometry on the surface of other metals demonstrating special effects, construction of regular and periodical structures, lattices etc.).

Methods of preparation and, more importantly, manipulation with small objects, molecules and atoms (e.g. scanning tunnel microscopy, electron microscopy, epitaxy etc.) are called nanotechnology.

Nanoproducts are therefore 1, 2 or 3 – dimensional restricted spatial structures surrounded by or filled by some form of mater.

View on the subject according to our position will be explained.

Nanoparticles and nanostructures share similar phenomena:

- **unique physical and chemical properties quite different from those found in macrocrystalline material (e.g. bulk material).**

Iron Fe is soluble and yellow.

Semiconductor like Cd_3As_2 is red (can be also yellow), exhibits strong luminescence, and is soluble.

Carbon C is red and soluble.

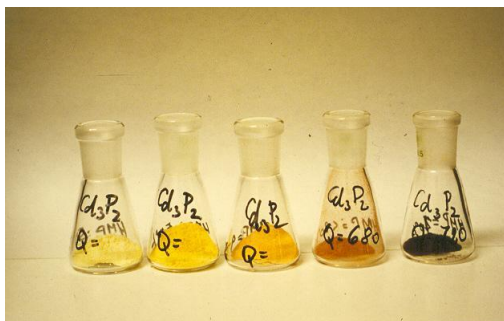
Silicon Si is yellowish, exhibits strong luminescence, and is soluble in organic solvents.

And so on.

Nanoparticles of Cd_3P_2 – luminescence



in UV light



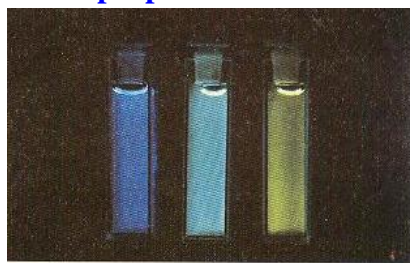
in day light

Luminescence of nanoparticles Cd_3As_2 in aqueous solutions in UV light



Increasing particles size from left to right

Luminescence of nanoparticles ZnO in propanol-2 sol. in UV light



Priority is the goal.

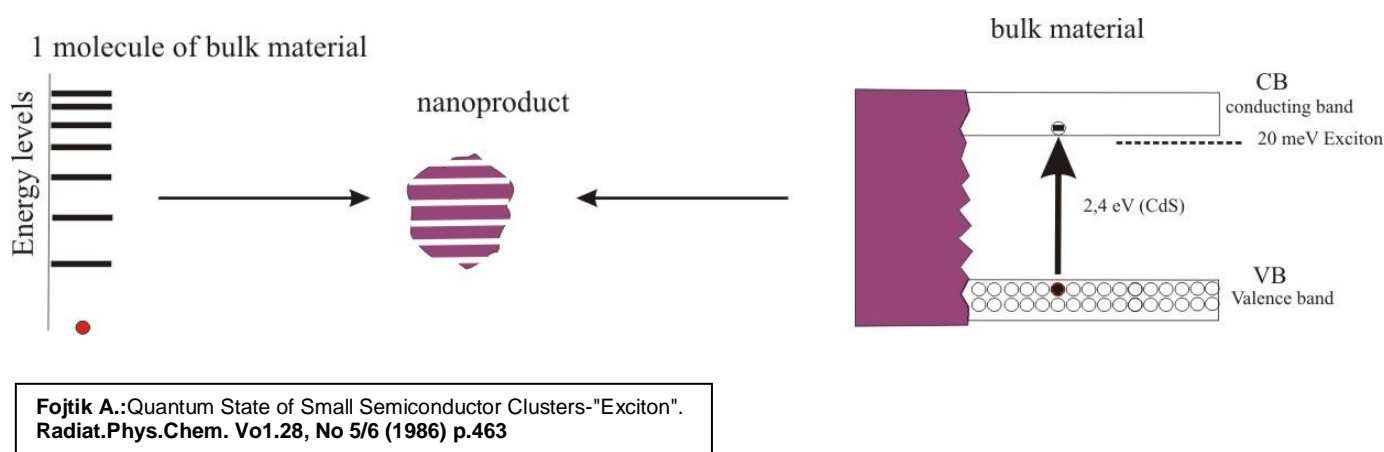
Ways of their preparation are of less importance.

Unique qualities come from their physical origin and that is done by their size.

Using another words:

- they are determined by the spatial extent in which they are created.

Creation of nanoproducts



The size effects are generally described by the well-known quantum mechanics of a „particle in a box“ .

The **electron** and **positive hole** are confined to potential wells of small dimension a this leads to a quantization of the energy levels (which in the bulk material constitute virtual continua in the **conduction** and **valence band**, respectively). The phenomena arise when the size of the particle becomes comparable to the DeBroglie wavelength of the carriers.

The quantization effects for an electron in an evacuated box become significant at box dimensions of some 0,1 nm. However, in the colloidal particles the effects can already be seen at a much larger particle size(1).

The reason for this lies in the fact that the effective mass of a charge carrier, which moves in the periodic array of the constituents of the crystal lattice, is generally much lower than the mass of an electron in free space.

This results in a larger DeBroglie wavelength.

The smaller the effective mass of the charge carriers, the more pronounced are the optical size effects. The effects can lead to drastic changes in the color of a material, the color of its luminescence, and its catalytic properties.

To indicate that a material has unusual properties as compared to those of macrocrystalline material we proposed using the prefix Q before the chemical formula (1-4).

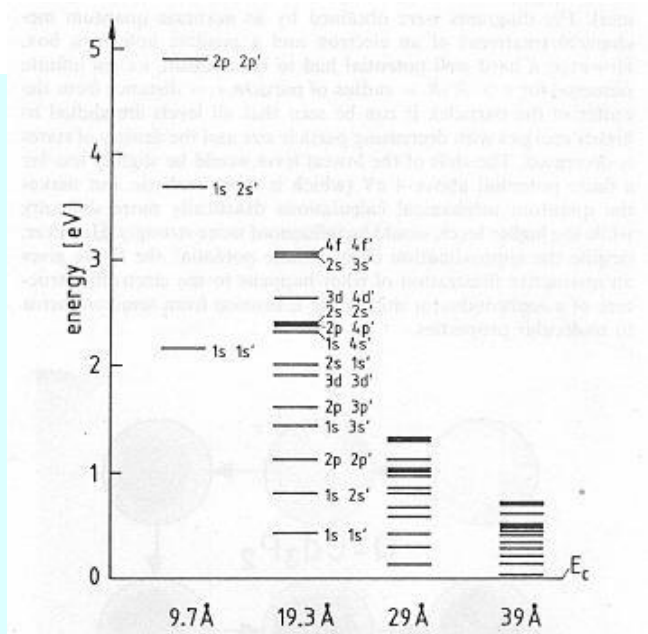
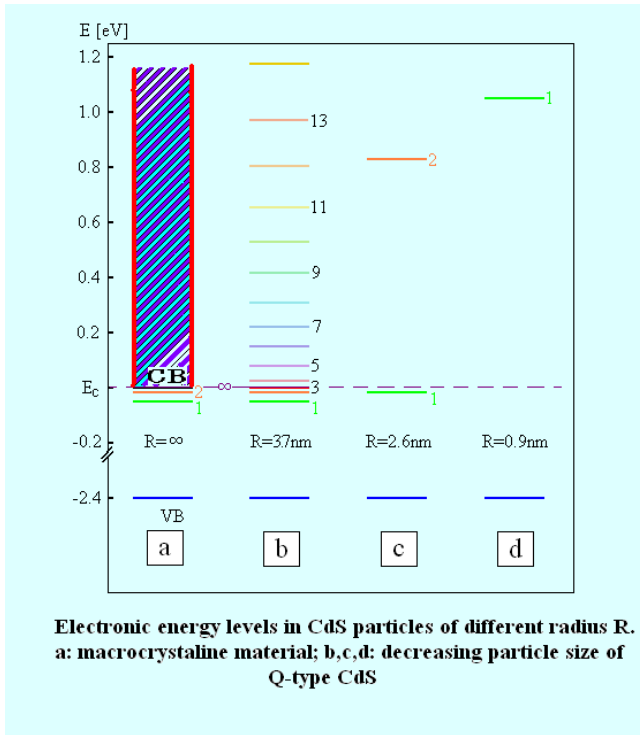
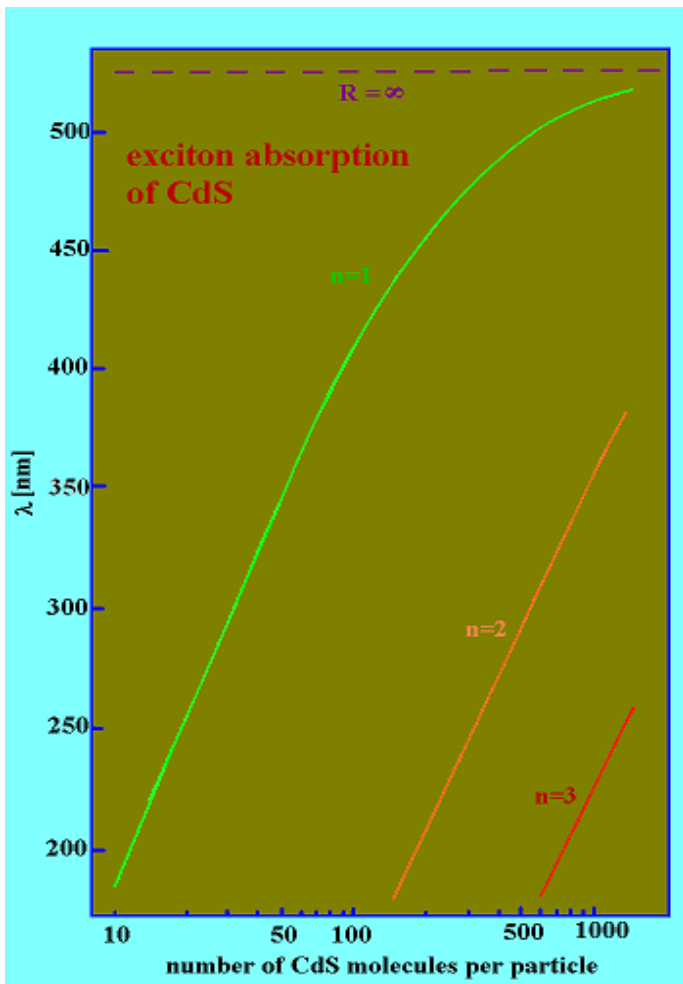


Fig. 5
Energy levels of excitonic states in CdS particles of various radii. Zero: position of the lower edge E_c of the conduction band in macrocrystalline CdS. Effective masses of electrons and holes $0.19 m_0$ and $0.8 m_0$ respectively. The letters with a prime designate the quantum state of the hole



Maxwell-Boltzmann

$$E = \frac{3}{2} kT \quad E_{300K} = 0.04 eV$$

where T is temperature in K
and $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

DeBroglie - duality of particles

$$\lambda = \frac{h}{\sqrt{2mE}}$$

where λ is wavelength of thermal electron at 300 K,

E is mean energy of the electron,

$h = 6.63 \times 10^{-34} \text{ Js}$ and

$m = 9.1 \times 10^{-31} \text{ kg}$

$$E = [eV] \times 1.60 \times 10^{-19} \text{ J eV}^{-1}$$

$$\lambda = 61.5 \text{ Å}$$

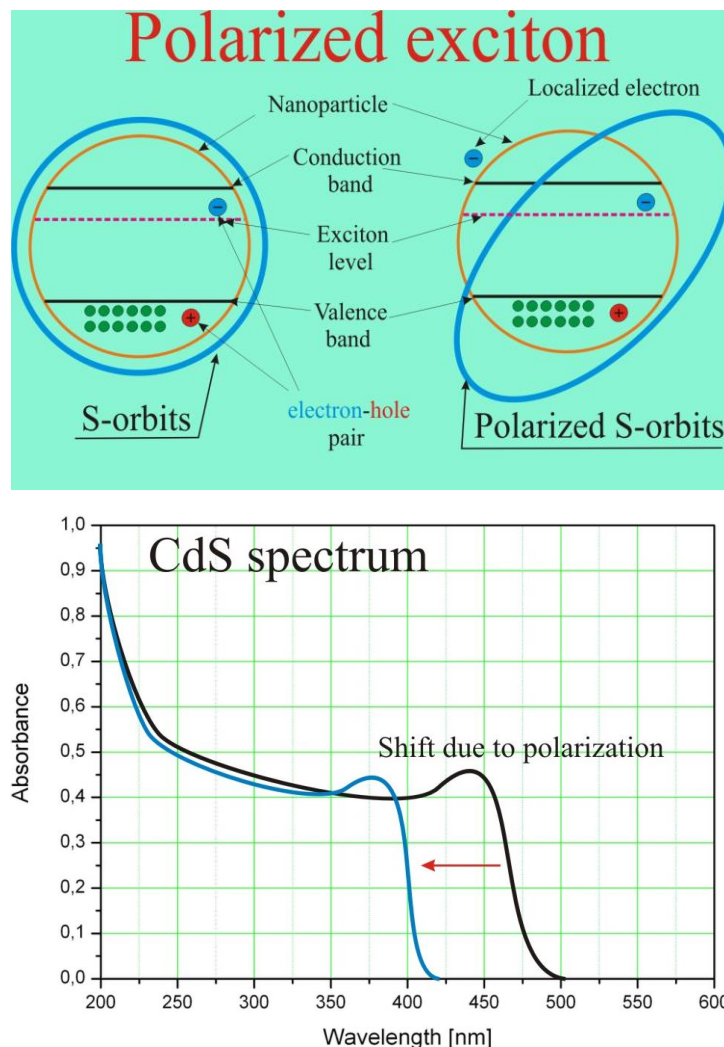
Semiconducting systems of low dimensionality, so-called superlattices, are frequently used in the field of micro-electronics.

Potential wells for both conduction band electrons and valence band holes are formed, and the position of these bands depends on the thickness of the wells and barriers.

As the quantization occurs only in one dimension in these structures, the shifts of the electronic levels are only of the order of 0,1 eV, while the shifts in the colloidal particles, where quantization is operative in all three dimensions, can amount to several eV.

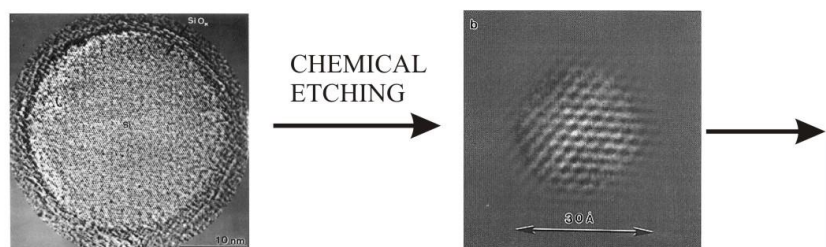
It may be mentioned that size quantization effects in the optical spectrum of CdS were observed for tiny crystals grown (2-5)

The fact that the absorption spectrum of Q-particles (f.e. CdS) changes when electrons are produced on it may be regarded as a non-linear optical effect, i.e. a dependence of the absorption coefficient on the light intensity. (Polarisation of excitons or Q-particles).

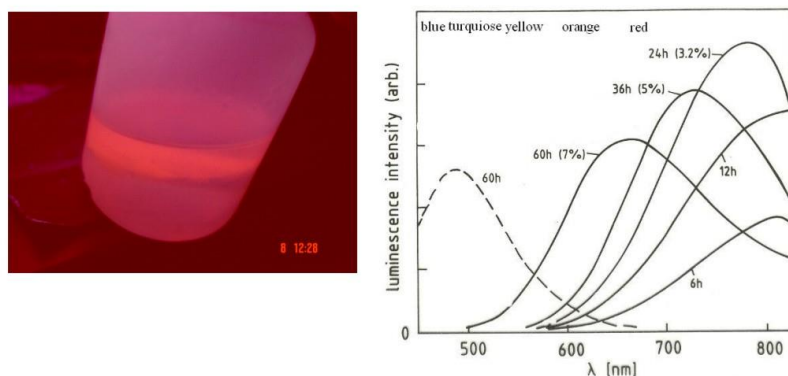


Other non-linear effects, which are caused by the changes in refractive index with light intensity, are being investigated intensively.

SILICON NANOPARTICLES



Luminescence of Si nanoparticles after etching



LUMINESCENCE SILICON NANOPARTICLES IN CYCLOHEXAN SOLUTION

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