

THE SEMICONDUCTING NANOCRYSTALS

A.S. ABBASOV, S.I. MEKHTIYEVA

Institute of Physics of Azerbaijan National Academy of Sciences

H. Javid, av., 33, Baku, 370143

The paper reviews a recent state of physico-chemical studying of semiconducting nanocrystals. There have been highlighted the major factors to condition special physico-chemical properties of semiconducting nanocrystals. It has been revealed a difference in chemical conversions on their surface and in the volume dealt with a dimensional factor. Most of nanoparticle surface atoms determine melting temperature and pressure as the conditions under which semiconductor lattice rearrangement occurs depending on the size of nanoparticle.

Non-linear optical effects and dependence of optical characteristics and physico-chemical properties versus the size are brought about by comparability of the size of nanoparticles and the radius of delocalization of charge carrier.

INTRODUCTION

As known the properties of semiconductors containing a macroscopic number of atoms do not depend their size. During the past few years it has been shown that at a characteristic size of semiconducting particles <10 nm many of their physico-chemical properties vary. It is stipulated by the fact that in the semiconductors the energy of intermolecular interaction is high and the crystal might be considered as a whole big molecule in the description of electronic properties.

Crystal excitation leads to the formation of light-bound electron-hole pair whose delocalization area might significantly outsize a constant of crystal lattice. The given decrease in the size of crystal has an effect on its electronic properties.

Supersmall crystals are known in the literature as nanoparticles, nanocrystals or the quantum-sized particles.

Investigations of nanocrystals have brought to light a line of their peculiar properties to be of a great interest.

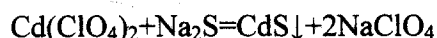
Dependence of electronic excitation radiation life time versus size, melting temperature, pressure necessary for rearrangement of crystal structure characteristic physico-chemical properties are conditioned by three major reasons: firstly, the size of nanoparticles is comparable with a Bohr radius of excitons in the semiconductors. This determines optical, luminescent and another properties of nanoparticales.

Secondly, for nanoparticles a number of atoms to be on the surface accounts for a quite significant part of the total. So, for 6 nm-sized CdSe about 20% of atoms is situated on the surface. Surface atoms contribute to the thermodynamic properties, and determine a structural transition and melting temperature; thirdly, own size of nanoparticles is comparable with the size of molecules which determines the thermodynamics and kinetics of chemical conversions on the surface. To date the following nanoparticles have been synthesized and studied: CdSe, CdC, MoC, HgC, ZnO, SiO₂, etc. For some nanoparticles there have been studied structure of electronic zones, electrochemical and thermal properties. The present paper overviews the methods of synthesis, quantum dimensional effects characteristic for semiconducting nanoparticles.

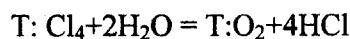
METHODS OF SYNTHESIS

Nanocrystals are produced by the method of chemical synthesis in colloidal solutions, polymers, glasses, zeolites, micelles [1-4]. The simplest method is the synthesis from initial reagents in solution by means of interrupting a reaction at a certain moment of time. Nanoparticles of metal sulfides

are synthesized by the reaction between water-soluble salt of metal and H₂S or Na₂S in the presence of stabilizer-sodium metaphosphate:



In the course of reaction the growth of nanoparticle CdS is interrupted as pH of solution is increased. Nanoparticles TiO₂ are formed in the hydrolysis of titanium tetrachloride:



Large-sized nanoparticles are synthesized by adding extra molecules to an initial cluster stabilized in a solution with organic ligands. It is normally assumed that nanoparticles, containing some hundreds of atoms have spherical or ellipsoid shape and sometimes have distinct faces similar to macroscopic crystals.

Shape and size control is hold by the methods of electronic microscopy.

A gas-phase synthesis of nanoparticles T:O₂ and Si is submitted in [5] with a yield ~70%

In [6,7] there has been suggested the method of synthesis of semiconducting nanoparticles by of metal pulsed laser evaporation in the chamber containing a necessary amount of gas-reagent by means of controlled nanoparticles condensation on the carrier.

The given method is a modification of the method of synthesis in a diffusion chamber and enables the synthesis of nanoparticles with mixed molecular composition-oxides, nitrides carbides and their mixtures. By changing the composition of gases in a chamber and by varying a temperature gradient and the power of laser pulse, it is possible to control both composition and size of nanoparticles. Nanoparticles might also be synthesized by ultrasonic treatment of colloidal solutions of large particles of semiconductors. Nanoparticles of layered semiconductors are formed as a result of large particles dissolution in an appropriate solvent. MoS₂-type layered semiconductors are distinguished for Van der Waals force between separate layers S-Mo-S [8]. During the process of dissolution the molecules of solvent penetrate into the space between the layers of semiconductor and destroy large particles therein. With respect to MoS₂ the process proceeds until a bilayered particle is formed. The further destruction of layers is not observed because the formation of monolayered particle is accompanied by an increase of free energy.

The ultrasonic treatment of dispersed system with large particles also leads to the formation of nanoparticles MoS₂,

WS₂, PbJ₂, Fe₂O₃ [10]. In respect to PbJ₂-type layered semiconductors there have been observed discoid-nanocrystals featuring discrete magic "disc size" [11]. It is assumed that, in this case, a stable particle-crystallite holding a hexagonal symmetry of macroscopic crystal consists of two layers of iodine of seven atoms and of two layers of lead MoS₂ nanoparticles are an analogous structure.

There is a great interest shown to thin films of semiconducting nanoparticles, which are synthesized by means of the precipitation of previously synthesized nanoparticles from colloidal solutions onto the carriers, by means of direct precipitation of semiconductor molecules onto the carrier and by means of oxidative hydrolysis of metal salts at the anode.

Normally, a film thickness is 0, 1-1 μm.

Films of SnO₂, ZnO₃, WO₃, Fe₂O₃ have been synthesized

Oxidative hydrolysis of TiCl₃ at pH=2, 3 and potential of platinum anode leads to the formation of nanoparticles of 1-2nm in diameter on the surface of anode [12].

By the method of precipitation it is possible to form nanostructured films to contain nanoparticles of different semiconductors.

Another method of film synthesis consists of wetting of the plate with a deposited film of certain type of nanoparticles in a solution containing ions of metal followed by wetting in a solution with sulphide ions. The films containing ZnO and CdS have been synthesized by this way [13,14].

OPTICAL PROPERTIES VERSUS THE SIZE OF NANOPARTICLES

Change of excitation energy of semiconducting crystals when their small are sizes is seen obvious. The electron excitation energy of an isolated molecule normally highly exceeds interband transition energy in the macroscopic semiconductor. It means that in the transition from crystal to molecule there should be a certain size range within which a smooth change in crystal electron excitation energy from a smaller magnitude to a greater one to characterize a given molecule is observed. For the semiconducting crystals such the transition occurs over a nanometric range. For a variety of semiconductors, there has been shown the influence of the size of nanoparticles on the optical spectra.

In [7] the spectra for different-size nanoparticles CdSe have been represented and it has become clear that nanoparticles absorption spectrum shifts to a short-wave region with an increase in their size. Dependence of nanoparticle electron excitation minimum energy on the size could approximately be calculated if the correlation between the uncertainty (Δx) in position and the uncertainty (Δp) in momentum of an exciton in the macroscopic crystal and in nanoparticle

$$\Delta p \cdot \Delta x \geq \frac{\hbar}{2} \quad (1)$$

is taken into account.

The position of delocalized exciton in a periodic potential of the macroscopic crystal is not fixed, but the energy (E) and momentum (p = ħK) are strictly determined and at small (K)

$$E = \frac{\hbar^2 K^2}{2\mu}, \quad (2)$$

where μ is an exciton effective mass.

For nanoparticle the uncertainty in an exciton position depends on a nanoparticle characteristic size Δx=d. If one assumes that the ratio between the energy and momentum does not depend on the size of a particle, the energy of exciton will vary inversely with the square of nanoparticle characteristic size.

More rigorous analysis of the effect of the size of spherical nanoparticles upon an exciton excitation energy E_n leads to the following equation:

$$E_n = E_m + E_1 \quad (3)$$

where E_m is an interband transition energy in the macroscopic semiconductor; E₁ is the energy of an exciton localization on the nanoparticle

$$E_1 = \frac{\hbar^2 n^2}{8R^2 \mu} - \frac{1.78e^2}{\epsilon R} - 0.248E_R^X \quad (4)$$

n is integer number, R is the nanoparticle radius,

$$\mu = \left(m_e^{-1} + m_n^{-1} \right) \quad (5)$$

m_e and m_n are effective masses of electron and hole respectively; ε is a semiconductor dielectric permittivity semiconductor dielectric permeability; E_R^X is Rydberg effective energy. First term in the right hand side of the equation is a dominating one, the second one allows for a Coulomb interaction between an electron and hole inside the nanoparticle, third is responsible for a spatial correlation. The values n>1 in the equation are consistent with the transition of an exciton to the higher excited states. In the case of anisotropic semiconductors effective masses of electron and holes are direction-dependent: in view of anisotropy the equation takes more complicated form:

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8} \left(\frac{n_x^2}{\mu_x \alpha_x^2} + \frac{n_y^2}{\mu_y \alpha_y^2} + \frac{n_z^2}{\mu_z \alpha_z^2} \right) - \frac{1.78e^2}{\epsilon R} - 0.243E_R^X, \quad (6)$$

where n_x, n_y, n_z are integer numbers; μ_x, μ_y, μ_z are exciton effective masses along the corresponding directions; α_x, α_y, α_z are nanoparticle geometrical sizes. The nanoparticle exciton excitation energy is well described by function 1/R². The

given equation is frequently used to calculate the nanoparticle size:

$$KR = \frac{n}{\sqrt{8\mu E}} \quad (7)$$

Another manifestation of size effect in the optical characteristics of nanoparticles is found to be a short-wave shift of the optical spectrum of nanoparticles under "the placing" an excess electron on them. There may be three reasons to explain the given shift: firstly, an increase in the energy of an exciton as a result of the effect of the excess electron electric field; secondly, the effect of low vacant state occupation by the excess electron, much energy is needed to excite the electron to a higher state; thirdly, a decrease in the power of exciton transition oscillator because due to the effect of electrons and holes trapped. The recombination of light-generated charges leads to nanoparticles luminescence. With an increase in their size, a short-wave shift is observed under these conditions. The luminescence of ZnO, ZnS, CdS, CdSe has been comprehensively studied. One more manifestation of quantum size effect is the growth of oscillator strength fixed on volume of an excitonic absorption. This growth occurs with the size decrease with an increase in integral of electron and hole wave functions overlapping in parallel with a decrease in the size of nanoparticles [16-17].

DEPENDENCE OF THERMODYNAMIC PROPERTIES ON NANOPARTICLES SIZES

A big number of atoms in nanoparticles find themselves on the surface and increase with a decrease of the nanoparticles size. Their contribution to the energy of nanocrystal is high enough. Because of that there is a regular dependence of melting temperature of nanoparticles on their sizes.

In the case of CdS nanoparticles:

1.5 nm-600 K; 2 nm-100 K; 3.7 nm-1200 K [18-20]. As known, liquid surface energy is lower than that of crystal.

A decrease in the size of nanoparticles leads to an increase in surface energy, and consequently, to a decrease in melting temperature.

The pressure may change the geometry of the crystal lattice of macroscopic crystal to come to a tighter packing (the same is observed in the case of nanocrystals). The pressure brought to bear on CdS nanocrystal CdS with a structure of wurtzite (tetrahedron coordination) results in the change of structure to face-centered cubic one. As a result, less ordered surface with high energy is formed. In the case of JnP, CdS, CdSe and Si an increase in the pressure necessary to change

the geometry of crystal lattice with a decrease in the size has been observed. This phenomenon is characteristic of nanocrystals, which account for a great portion of the surface centres.

The colloidal solutions of nanocrystals are found to be useful in the demonstration of their application in photocatalysts. It should be noted that their practical usage is complicated due to the necessity of separating nanoparticles from solution after the completion of a photocatalytic process. In this aspect thin layers of nanoparticles adsorbed on the film to consist of heteronanoparticles are seen more promising. This expands the range of spectral sensitivity referred to wide-band semiconductors and increases a quantum effect of photoseparation with respect to the charges. Porous films of nanoparticles display a high adsorbability.

The application of the above-mentioned features allows to increase their photocatalytic effects at the cost of films sensibilization to the visible region of spectrum [21,22].

CONCLUSIONS

From the present review of papers dedicated to the investigation of semiconducting nanocrystals, it follows that their extraordinary physicochemical characteristics are caused by the following factors:

The size of nanoparticles is comparable with that of molecules and this defines the difference between chemical conversions on their surfaces and in the bulk.

The number of atoms on the surface of nanoparticles accounts for a great amount of the total what has an effect on the thermodynamic properties of the particles. This condition defines dependence of melting temperature and pressure, at which the rearrangement of semiconductor crystal lattice occurs, on its size.

Non-linear optical effect and dependence of execution transition energy, oscillator strength and other characteristics on the size of nanoparticles are brought about by comparability of the size of nanoparticles and the radius of delocalization of charge carriers.

At present the development of the methods of nanoparticles synthesis, integrated study of their physicochemical properties, introduction of results obtained in electronics, ecology, etc. are of a great interest.

- [1] L.E. Drus. J.Chet., 1984, 80, 4403.
- [2] Y. Wang. Opt. Commun., 1987, 61,233.
- [3] N.F. Borreli. J.Appl.Phys., 1987, 61, 53999.
- [4] M. Visca, E. Matijevic. J.Colloid Interface Sci., 1979, 68, 308.
- [5] M.W. Peterson. J.Phys. Chem., 1988, 92, 1400.
- [6] J. Kavan, T. Stot. J.Phys. Chem., 1993, 97, 9493.
- [7] S. Hotchadani, P.V. Kamat. J.Phys. Chem., 1992, 96, 6834.
- [8] A.L. Efros. The Physics and technics of semiconductors. 1982, 16, 1209.
- [9] C.R. Berry. Phys. Rev., 1967, 161, 948.
- [10] Y. Kayanuma. Phys. Rev., 1988, 38, 9797.
- [11] T.S. Moss. Proc. Phys. Soc. B., 1954, 76, 775.
- [12] W.J. Albery, G.T. Brown. J.Chem.Soc., 1985, 1, 81, 1999.
- [13] A. Henglun, A. Kumar. Chem. Phys.Left., 1986, 132, 133.
- [14] E. Hilinski. Phys.Rev., 1954, 93, 632.
- [15] W.G. Becker, A.J. Bard. J.Phys. Chem., 1983, 87, 4888.
- [16] R.F. Khairutdinov. Chem., 1993, v.24, №2.
- [17] N.M. Dimitrievic. J.Chem., 1987, 83, 1193.
- [18] J. Crysochoos. J.Phys. Chem., 1992, 96, 2868.
- [19] M. Haase, A.P. Alivisatos. J.Phys. Chem., 1971, 96, 6756.
- [20] A.P. Alivisatos. J.Phys. Chem., 1996, 100, 13226.
- [21] R.F. Khairutdinov, N. Serphone. Prog. React. Kinet., 1996, 21, 1.

THE SEMICONDUCTING NANOCRYSTALS

A.S. Abbasov, S.I. Mehdiyeva

YARIMKEÇİRİCİ MONOKRİSTALLAR

Nanozərrəciklərin fiziki-kimyəvi tədqiqatlarının perspektivləri nəzərdən keçirilib. Yarımkəçiricilərdə nanozərrəciklərin qeyri-adi xassələrinin əsas faktorları təyin edilib. Nanozərrəciklərin termodinamik xassələri, (təzyiq, ərimə temperaturu) onların ölçüsündən asılılığı aydınlaşdırılıb. Qeyri-xətti effektlərin əmələ gəlməsi və onların nanozərrəciklərin ölçüsündən asılılığının səbəbkarı nanozərrəciklərin ölçülərinin uyğunluğudur.

A.C. Аббасов, С.И. Мехтиева

ПОЛУПРОВОДНИКОВЫЕ КРИСТАЛЛЫ

Рассмотрено состояние исследования физико-химических характеристик нанокристаллов. Определены основные факторы, обуславливающие необычные их свойства.

Выяснена зависимость термодинамических свойств (давление, температура плавления) от размеров нанокристаллов. Обсуждены возникновение нелинейных эффектов и их зависимость от размеров нанокристаллов.

Received: 21.09.01