

O.V. Kuzyk¹, O.O. Dan'kiv¹, I.D. Stolyarchuk¹, R.M. Peleshchak^{1,2},
Yu.O. Uhryn¹, V.A. Kuhivchak¹

The influence of hydrostatic pressure on the synthesis of colloidal core-shell quantum dots with the mismatch of lattice parameters

¹Ivan Franko Drohobych State Pedagogical University, Drohobych, Ukraine, olehkuzyk@dspu.edu.ua;

²Lviv Polytechnic National University, Lviv, Ukraine

The theory of the synthesis of colloidal quantum dots of the core-shell type with the mismatch of lattice parameters of the contacting materials which are subjected to additional external hydrostatic pressure has been developed. The proposed model takes into account the influence of hydrostatic pressure on the homogeneous nucleation of the shell material and its heteroepitaxial growth on the core surface. Within the framework of the developed model, the regularities of change in the homogeneous nucleation of colloidal ZnS nanoparticles, that is the material of the shell, and the heteroepitaxial growth of the ZnS shell on the CdSe core under the action of external pressure have been established. It was found that such hydrostatic pressure complicates the homogeneous formation of nanoparticles of the shell material (increases the critical radius, at exceeding which the growth of nanoparticles and the potential barrier for their nucleation are possible) and, on the contrary, practically does not change the conditions of heteroepitaxial growth of the shell on the core.

Keywords: core-shell quantum dot, hydrostatic pressure, nucleation.

Received 15 April 2024; Accepted 30 July 2024.

Introduction

The semiconductor quantum dots (QDs) have a high photoluminescence quantum yield and are a promising material for use in photonics, medicine, and other fields. The colloidal QDs have a number of advantages compared to QDs obtained by molecular beam epitaxy methods. One of these advantages is the ease of manufacture and the low cost of the technological process [1, 2]. Such QDs have a regulated band gap which depends on size, that allows to precisely control the wavelength of radiation. Among other QDs, the A²B⁶ semiconductor QDs should be highlighted, which have good fluorescent properties: high quantum yield, photostability and regulated radiation spectra [3].

But QDs have a high density of traps that act as centers of non-radiative carrier recombination. Thus, they reduce the intensity of photoluminescence due to the transfer of electric charge from QD to the molecule of drug preparation [4]. One of the methods to solve this problem

is to create the QD with the protective shell. Also, the protective shell significantly reduces the toxicity of cadmium-containing quantum dots [4, 5].

One of the most common core-shell structures are the CdSe/ZnS nanocrystals, which are type-I heterostructures. Such a heterostructure makes it possible to effectively localize both electron and hole in the core. However, the mismatch of crystal lattice parameters (~11 %) with an increase in thickness of the shell leads to an increase in mechanical strains and, as result, to the appearance of defects at the interface. Therefore, as a rule, the optimal number of monolayers of the shell in CdSe/ZnS QDs, for which the highest quantum efficiency is observed, does not exceed two. The maximum quantum efficiency of the CdSe QDs can be achieved by creating a multilayer structure with buffer layers of CdS and ZnS, which reduce mechanical strains in the structure. The shell is epitaxially grown in solution, and the required amount of precursors is determined by the volume of material for each monolayer.

Despite significant successes in the synthesis of colloidal quantum dots of the core-shell type [6, 7], their quality has not yet reached the quality of nanocrystals with a simple core. Foremost, it concerns the uniformity of the structure, controllability of size and concentration. In [8], two main critical problems for preserving the size distribution of nanocrystals during shell growth are singled out, which have not been fully resolved to date. This is the elimination of homogeneous nucleation of shell materials with subsequent coalescence of homogeneous nanoparticles and ensuring layer-by-layer growth of shells on all cores in solution with the formation of layers of the shell of the same thickness around each core. To fulfill these conditions, the reactivity of the precursors must be weak enough to prevent independent nucleation, but strong enough to promote epitaxial growth around existing core nanocrystals.

The conditions for the formation of nanoparticles (NPs) are significantly affected by deformation effects due to the non-zero volume of intrinsic defects and impurities [9], the mismatch of lattice parameters of the contacting materials [10], as well as the ultrasonic wave [11].

In this paper, we have considered the process of heteroepitaxial growth of the ZnS shell on the surface of the CdSe core and the homogeneous nucleation of ZnS nanoparticles in the colloidal solution which are subject to external comprehensive compression. It is assumed that such hydrostatic pressure should complicate the independent formation of nanoparticles of the shell material and, conversely, practically not change the conditions of heteroepitaxial growth of the shell on the core.

I. The model

Consider the initial stage of the growth of the heteroepitaxial ZnS layer on the surface of the CdSe core and the separate independent nucleation of ZnS nanoparticles in the colloidal solution. The latter is a negative factor during the synthesis of QD of the core-

shell type, which leads to a decrease in the concentration of the monomer from which the shell is formed. As a result, the concentration of colloidal QDs with a shell decreases, as well as the shells of different thicknesses are formed on different cores. Let's analyze how the hydrostatic pressure in the colloidal solution can affect these processes. To do this, we separately consider the homogeneous nucleation of ZnS nanoparticles and the heteroepitaxial growth of the ZnS shell under the action of hydrostatic pressure within the classical theory.

1.1. The homogeneous nucleation of colloidal ZnS nanoparticles under the action of hydrostatic pressure

According to the classical theory of nanoparticle nucleation [12, 13], the nucleation occurs spontaneously. In a supersaturated solution, molecules of a dissolved substance crystallize, forming nuclei of nanoparticles. The rate of formation of nanoparticles is proportional to the relative supersaturation of the solution s . When nanoparticles with radius r are nucleated, a new interface between the solid and liquid phases appears. This leads to an increase in the free energy of the researched system by an amount

$$\Delta G_s = 4\pi r^2 \gamma_s, \quad (1)$$

where γ_s is the surface energy of the material of the ZnS shell.

The additional hydrostatic pressure P also leads to an increase in the free energy by an amount

$$\Delta G_p = \frac{4}{3} \pi r^3 P. \quad (2)$$

At the same time, due to a decrease in the chemical potential (molecules pass from a liquid to a solid), a decrease in free energy is observed:

$$\Delta G_v = -\frac{4}{3} \pi r^3 \frac{k_B T \ln s}{V}, \quad (3)$$

where V is the molecular volume of the solid phase [13].

Thus, the change in free energy during the homogeneous growth of ZnS nanocrystals is determined by the relation:

$$\Delta G = \Delta G_s + \Delta G_v + \Delta G_p = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 P - \frac{4}{3} \pi r^3 \frac{k_B T \ln s}{V}. \quad (4)$$

Analysis of the dependence of $\Delta G(r)$ shows that such a function has a maximum at

$$r_{pc} = \frac{2\gamma V}{k_B T \ln s - PV}. \quad (5)$$

A process that leads to a decrease in free energy is energetically beneficial (Fig. 1). That is, only nanocrystals with a radius greater than r_{pc} (greater than r_c in the absence of additional hydrostatic pressure) can grow.

Fig. 1 shows the dependence of the change in the free energy of a ZnS nanoparticle on its radius in the colloidal solution exposed to external hydrostatic pressure at different temperature values. The calculations were carried out at $s = 4$ for the parameters of ZnS, which are listed in Table 1 [14, 15].

An increase in the hydrostatic pressure in the colloidal

solution leads to a significant increase in the critical radius of nanoparticles, at exceeding which their homogeneous growth is possible. Thus, at a temperature of 400 K, an increase in hydrostatic pressure to 0.9 kbar leads to an increase in the critical radius of colloidal ZnS nanoparticle from 5 nm to 15 nm (Fig. 1a). Also, the presence of external pressure leads to an increase in ΔG_{max} from 100 eV (in the absence of pressure) to 1800 eV (at pressure of 0.9 kbar). And this will lead to a significant decrease in

the nucleation rate $\frac{dN}{dt} = A_0 e^{-\frac{\Delta G_{max}}{k_B T}}$ and, accordingly, in the

concentration of ZnS nanoparticles in the colloidal solution. Thus, both results of the influence of hydrostatic pressure on the nucleation of colloidal nanoparticles (increasing the critical size for the nucleation of ZnS nanoparticles and increasing their nucleation energy) will

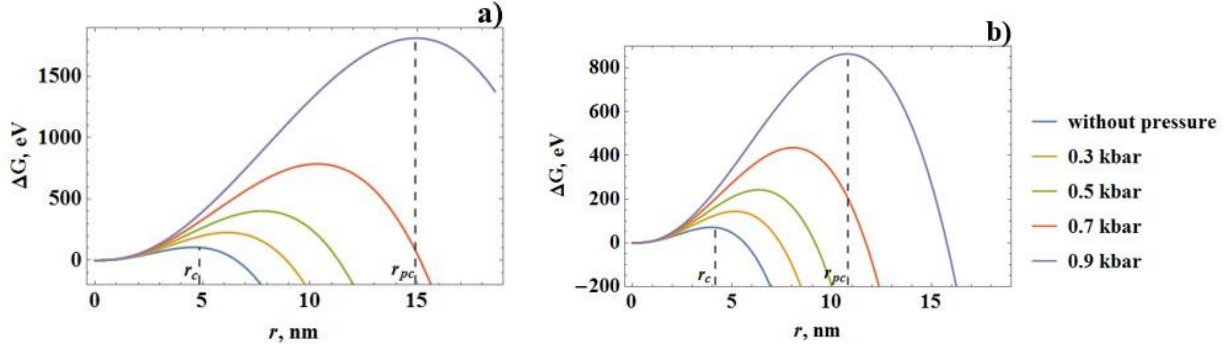


Fig. 1. The dependence of the change in the free energy of a ZnS nanoparticle at temperatures of 400 K (a), 450 K (b) and at different values of external hydrostatic pressure.

lead to a decrease in the probability of homogeneous growth of ZnS nanoparticles. And ZnS is the planned material of the shell.

Table 1.

Parameters of CdSe and ZnS semiconductors

	$a^{(i)}$, nm	c_{11} , Mbar	c_{12} , Mbar	$\gamma_{bulk}^{(i)}$, J/m ²	V , nm ³
CdSe	0.6077	0.667	0.463	1.65	0.055
ZnS	0.54093	1.067	0.666	1.39	0.039

An increase in temperature slightly worsens this effect (Fig. 1b). Thus, at a temperature of 450 K, an increase in pressure to 0.9 kbar leads to an increase in the potential barrier of homogeneous nucleation of ZnS NPs to 850 eV. Similarly, the critical radius r_{pc} increases from 4.2 nm to 10.8 nm (Fig. 1b).

1.2. The heteroepitaxial growth of the ZnS layer on the surface of the CdSe core under the action of comprehensive compression

Consider the process of heterogeneous nucleation of the ZnS shell on the surface of the CdSe core under the action of hydrostatic pressure. The layer-by-layer heteroepitaxial growth is possible when

$$\gamma_A + \gamma_{AB} - \gamma_B < 0,$$

where γ_A is the surface energy of the deposited material; γ_{AB} is the energy of the A–B interface; γ_B is the surface energy of the substrate [16, 17].

In our case, in addition to mechanical strain caused by external pressure, mechanical strain also occurs in the CdSe/ZnS heterostructure due to the mismatch of lattice parameters of the contacting layers [10, 18]. Thus, the change in free energy during heteroepitaxial growth can be represented as follows:

$$\Delta G = 4\pi R_0^2 \gamma + \int_{\Omega} \sigma^{(i)} d\Omega - \frac{4}{3} \pi r^3 \frac{k_B T \ln s}{V}, \quad (6)$$

where $\gamma = \gamma^{(ZnS)} + \gamma_{AB} - \gamma^{(CdSe)}$; R_0 is the core radius; Ω is the volume of the spherical CdSe/ZnS nanocrystal; $\sigma^{(i)}$ is the mechanical strain of the materials of the heterosystem ($i = 1$ corresponds to the CdSe material, $i = 2$ corresponds to the ZnS material); in this case, r is the thickness of the growing shell.

In the CdSe/ZnS QDs, the lattice parameters

mismatch of contacting materials, the Laplace pressure caused by the surface curvature, and the external hydrostatic pressure are the source of elastic strains.

The lattice parameter of the CdSe core ($a^{(0)} = 6.077 \text{ \AA}$) is greater than that of the ZnS shell ($a^{(1)} = 5.40 \text{ \AA}$), so the CdSe core undergoes compressive deformation, and the ZnS shell undergoes stretching deformation.

The mechanical strain $\sigma_{rr}^{(i)}$ in the QD core and shell is determined by the formula:

$$\sigma_{rr}^{(i)} = \frac{E_i}{(1+\nu_i)(1-2\nu_i)} \left[(1-\nu_i) \varepsilon_{rr}^{(i)} + \nu_i (\varepsilon_{\phi\phi}^{(i)} + \varepsilon_{\theta\theta}^{(i)}) \right], \quad (7)$$

where ν_i , E_i are the Poisson's ratio and the Young's modulus, which are expressed in terms of elastic constants $c_{11}^{(i)}$ and $c_{12}^{(i)}$ corresponding materials.

In order to determine the components of the deformation tensor, it is necessary to find an explicit form of the displacements of the atoms $u_r^{(i)}$ in the core ($i = 1$) and the shell ($i = 2$). To do this, we will solve the equilibrium equation

$$\vec{\nabla} \operatorname{div} \vec{u} = 0, \quad (8)$$

with the following boundary conditions [14]:

$$\begin{cases} 4\pi R_0^2 (u_r^{(2)}(R_0) - u_r^{(1)}(R_0)) = \Delta V, \\ \sigma_{rr}^{(1)}(R_0) + P_L^{(1)}(R_0) = \sigma_{rr}^{(2)}(R_0) + P_L^{(2)}(R_0), \\ \sigma_{rr}^{(2)}(R_0 + r) + P_L^{(2)}(R_0 + r) = -P; \end{cases} \quad (9)$$

where $P_L^{(i)}(R) = \frac{2\gamma^{(i)}}{R}$ is the Laplacian pressure;

$\gamma^{(i)} = \frac{\gamma_{bulk}^{(i)}}{1 + \frac{2\delta}{R_i}}$ [18] is the surface energy of the core or

shell; $\Delta V = f \cdot 4\pi R_0^3$; f is the parameter of lattice mismatch in CdSe and ZnS nanomaterials.

In Fig. 2 shows the dependence of the change of free energy of the CdSe/ZnS colloidal heterosystem on the thickness of the growing shell at different values of temperature, core radius, and hydrostatic pressure.

As can be seen from Fig. 2, the hydrostatic pressure practically does not change the conditions of heteroepitaxial growth of the ZnS shell on the CdSe core

with a radius of 2 - 4 nm (Fig. 2a, b, c, d). In these cases, the hydrostatic pressure slightly increases the free energy, but this increase does not exceed 20 % under the given conditions at a temperature of 400 K and 15 % at a temperature of 450 K.

For larger cores (Fig. 2e), the heteroepitaxial growth of the shell in the presence of additional hydrostatic pressure at a temperature of 400 K can be interrupted at $r = 1.2$ nm. This is due to the fact that its further growth would lead to an increase in free energy, which is energetically disadvantageous. This phenomenon is caused by an increase in the mechanical strain in the shell when the radius of the core increases [14].

This effect can be leveled by increasing the temperature (Fig. 2f). Thus, at a temperature of 450 K and $R_0 = 6$ nm, the heteroepitaxial growth of the shell is

energetically advantageous at any pressure values up to 0.9 kbar. However, in this case, an increase in pressure leads to an increase in free energy by 30 %.

II. Discussion of results and Conclusions

The theory of the synthesis of core-shell colloidal QDs with the mismatch of lattice parameters of the contacting materials, that are subjected to additional external hydrostatic pressure, has been created. The proposed model takes into account the influence of hydrostatic pressure on the homogeneous nucleation of the shell material and its heteroepitaxial growth on the core. This theory takes into account the increase in elastic energy during heteroepitaxial growth of the shell, which

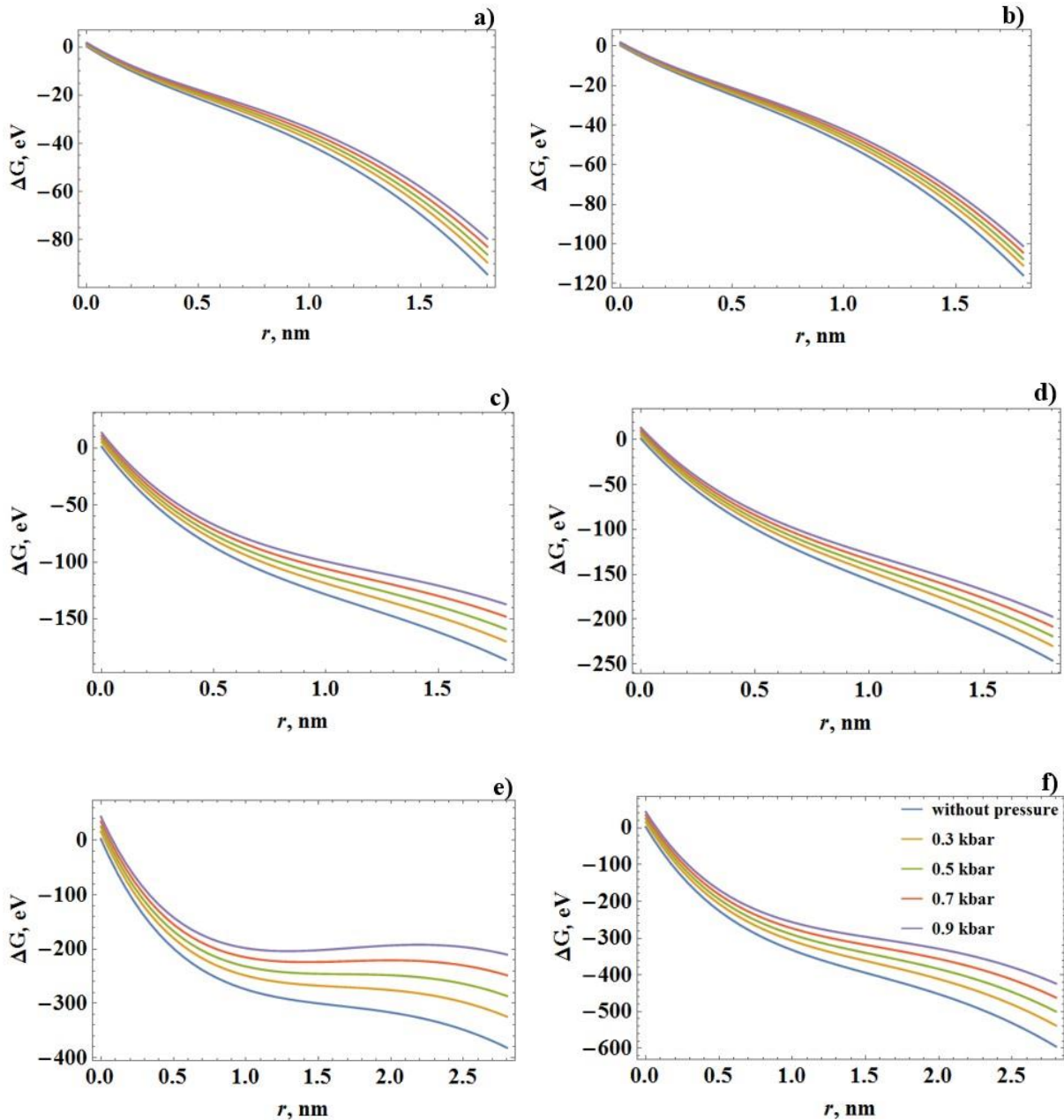


Fig. 2. The dependence of the change of free energy of the CdSe/ZnS colloidal heterosystem on the thickness of the growing shell at different values of hydrostatic pressure, temperature, and core radius: $T = 400$ K (a, c, e), $T = 450$ K (b, d, f), $R_0 = 2$ nm (a, b), $R_0 = 4$ nm (c, d), $R_0 = 6$ nm (e, f).

occurs both due to the mismatch of lattices of the contacting materials and the Laplace pressure, as well as the external hydrostatic pressure.

Within the framework of the developed model, the regularities of change in the homogeneous nucleation of colloidal ZnS NPs, which is the material of the shell, and the heteroepitaxial growth of the ZnS shell on the CdSe core under the action of external pressure have been established. The obtained results allow us to propose a method of eliminating the homogeneous nucleation of shell materials regardless of the core, which is a negative phenomenon in the formation of the core-shell heterostructure. This method is based on the following considerations. The creation of additional hydrostatic pressure in the colloidal solution practically makes homogeneous nucleation and growth of NPs of the shell material impossible due to an increase in the energy barrier and an increase in the critical radius, at exceeding which this growth is possible. This result is qualitatively consistent with the results of work [20], where it was shown that at low pressures (up to 10 kbar), the hydrostatic pressure prevents the coalescence of CdSe nanoparticles. On the contrary, the hydrostatic pressure practically does not change the conditions of heteroepitaxial growth of the shell under certain parameters. It was established that this effect is better manifested at small cores (up to 4 nm), on which the growth of the shell takes place, and at higher temperature.

Only colloidal nanoparticles with a radius greater than a certain critical value can grow homogeneously. It was established that an increase in the hydrostatic pressure in

the colloidal solution to 0.9 kbar leads to an increase in the critical radius of the colloidal ZnS nanoparticle from 5 nm to 15 nm and to an increase in the potential barrier of homogeneous nucleation from 100 eV to 1800 eV at temperature of 400 K. At the same time, under analogous conditions, the hydrostatic pressure leads to a slight increase in free energy (no more than 20 %) during the heterogeneous growth of the ZnS shell on the CdSe core. Thus, the creation of external pressure up to 1 kbar can solve the problem of undesirable homogeneous nucleation of shell materials and ensure the formation of shell layers of the same thickness around each core.

Acknowledgments

This work was supported by the Ministry of Education and Science of Ukraine (the state registration number of Project is 0124U001093).

Kuzyk O.V. – Candidate of Physical and Mathematical Sciences, Associate Professor;

Dan’kiv O.O. – Candidate of Physical and Mathematical Sciences, Associate Professor;

Stolyarchuk I.D. – Doctor of Physical and Mathematical Sciences, Professor, Dean of the Faculty of Physics, Mathematics, Economics and Innovative Technologies;

Peleshchak R.M. – Doctor of Physical and Mathematical Sciences, Professor;

Uhryn Yu.O. – Candidate of Physical and Mathematical Sciences, Associate Professor;

Kuhivchak V.A. – PhD student.

- [1] Z. Wang, Yu. Gu, F. Liu, W. Wu, *Facile synthesis of wide bandgap ZrS₂ colloidal quantum dots for solution processed solar-blind UV photodetectors*, Chemical Communications, 59(92), 13771 (2023); (<https://doi.org/10.1039/d3cc03594h>).
- [2] K. Agarwal, H. Rai, S. Mondal, *Quantum dots: an overview of synthesis, properties, and applications*, Mater. Res. Express, 10, 062001 (2023); (<https://doi.org/10.1088/2053-1591/acda17>).
- [3] U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, T. Nann, *Quantum dots versus organic dyes as fluorescent labels*, Nature Methods, 5(9), 763 (2008); (<https://doi.org/10.1038/nmeth.1248>).
- [4] B. Gidwani, V. Sahu, S.S. Shukla, R. Pandey, V. Joshi, *Quantum dots: Prospectives, toxicity, advances and applications*, Journal of Drug Delivery Science and Technology, 61, 102308 (2021); (<https://doi.org/10.1016/j.jddst.2020.102308>).
- [5] S. Filali, F. Pirot, P. Miossec, *Biological Applications and Toxicity Minimization of Semiconductor Quantum Dots*, Trends in Biotechnology, 38(2), 163 (2020); (<https://doi.org/10.1016/j.tibtech.2019.07.013>).
- [6] A. Sahu, D. Kumar, *Core-shell quantum dots: A review on classification, materials, application, and theoretical modeling*, Journal of Alloys and Compounds, 924, 166508 (2022); (<https://doi.org/10.1016/j.jallcom.2022.166508>).
- [7] J. Li, H. Zheng, Z. Zheng, H. Rong, Z. Zeng, H. Zeng, *Synthesis of CdSe and CdSe/ZnS Quantum Dots with Tunable Crystal Structure and Photoluminescent Properties*, Nanomaterials, 12, 2969 (2022); (<https://doi.org/10.3390/nano12172969>).
- [8] J.J. Li, Y.A. Wang, W. Guo, J.C. Keay, T.D. Mishima, M.B. Johnson, X. Peng, *Large-Scale Synthesis of Nearly Monodisperse CdSe/CdS Core/Shell Nanocrystals Using Air-Stable Reagents via Successive Ion Layer Adsorption and Reaction*, J. Am. Chem. Soc., 125(41), 12567 (2003); (<https://doi.org/10.1021/ja0363563>).
- [9] O. Kuzyk, O. Dan’kiv, I. Stolyarchuk, R. Peleshchak, *The deformation effects in isovalent doping of CdSe quantum dots with a multilayer shell for their biomedical applications*, Appl Nanosci., 13, 7007 (2023); (<https://doi.org/10.1007/s13204-023-02830-5>).
- [10] H.S. Pisheh, N. Gheshlaghi, H. Ünlü, *The effects of strain and spacer layer in CdSe/CdS/ZnS and CdSe/ZnS/CdS core/shell quantum dots*, Physica E: Low-dimensional Systems and Nanostructures, 85, 334 (2017); (<https://doi.org/10.1016/j.physe.2016.07.007>).
- [11] M.H. Entezari, N. Ghows, *Micro-emulsion under ultrasound facilitates the fast synthesis of quantum dots of CdS at low temperature*, Ultrasonics Sonochemistry, 18(1), 127 (2011); (<https://doi.org/10.1016/j.ultsonch.2010.04.001>).

- [12] D. Kashchiev, *Multicomponent nucleation: Thermodynamically consistent description of the nucleation work*, J. Chem. Phys., 120, 3749 (2004); (<https://doi.org/10.1063/1.1643711>).
- [13] N.T.K. Thanh, N. Maclean, S. Mahiddine, *Mechanisms of Nucleation and Growth of Nanoparticles in Solution*, Chem. Rev., 114(15), 7610 (2014); (<https://pubs.acs.org/doi/10.1021/cr400544s>).
- [14] O.V. Kuzyk, O.O. Dan'kiv, R.M. Peleshchak, I.D. Stolyarchuk, *Baric properties of CdSe-core / ZnS/CdS/ZnS-multilayer shell quantum dots*, Physica E: Low-dimensional Systems and Nanostructures, 143, 115381 (2022); (<https://doi.org/10.1016/j.physe.2022.115381>).
- [15] C.G. van de Walle, *Band lineups and deformation potentials in the model-solid theory*, Phys. Rev. B., 39(3), 1871 (1989); (<https://doi.org/10.1103/PhysRevB.39.1871>).
- [16] J. Johansson, *Heteroepitaxial growth modes revisited*, CrystEngComm, 25, 6671 (2023); (<https://doi.org/10.1039/D3CE00664F>).
- [17] L. Carbonea, P.D. Cozzoli, *Colloidal heterostructured nanocrystals: Synthesis and growth mechanisms*, Nano Today, 5, 449 (2010); (<https://doi.org/10.1016/j.nantod.2010.08.006>).
- [18] O. Kuzyk, O. Dan'kiv, R. Peleshchak, I. Stolyarchuk, *The deformation of spherical CdSe quantum dot with a multilayer shell*, Rom J Phys., 67, 607 (2022); (https://rjp.nipne.ro/2022_67_5-6/RomJPhys.67.607.pdf).
- [19] D. Vollath, F.D. Fischer, D. Holec, *Surface energy of nanoparticles – influence of particle size and structure*, Beilstein J. Nanotechnol., 9, 2265 (2018); (<https://doi.org/10.3762/bjnano.9.211>).
- [20] B. Li, K. Bian, X. Zhou, P. Lu, S. Liu, *Pressure compression of CdSe nanoparticles into luminescent nanowires*, Sci. Adv., 3(5), 1 (2017); (<https://doi.org/10.1126/sciadv.1602916>).

О.В. Кузык¹, О.О. Даньків¹, І.Д. Столярчук¹, Р.М. Пелещак^{1,2},
Ю.О. Угрин¹, В.А. Кувівчак¹

Вплив гідростатичного тиску на синтез колоїдних квантових точок ядро-оболонка з невідповідністю параметрів ґраток

¹Дрогобицький державний педагогічний університет імені Івана Франка, Дрогобич, Україна, olehkuzyk@dspu.edu.ua;
²Національний університет «Львівська політехніка», Львів, Україна

Розроблено теорію синтезу колоїдних квантових точок виду ядро-оболонка з невідповідністю параметрів ґраток контактуючих матеріалів, що піддаються додатковому зовнішньому гідростатичному тиску. Запропонована модель враховує вплив гідростатичного тиску на гомогенну нуклеацію матеріалу оболонки та її гетероепітаксійний ріст на поверхні ядра. В межах розробленої моделі встановлено закономірності зміни гомогенного зародження колоїдних наночастинок ZnS, що є матеріалом оболонки, та гетероепітаксійного росту оболонки ZnS на ядрі CdSe при дії зовнішнього тиску. Встановлено, що такий гідростатичний тиск ускладнює гомогенне формування наночастинок матеріалу оболонки (збільшує критичний радіус, при перевищенні якого можливий ріст наночастинок, та потенціальний бар'єр для їх нуклеації) і, навпаки, практично не змінює умови гетероепітаксійного росту оболонки на ядрі.

Ключові слова: квантова точка виду ядро-оболонка, гідростатичний тиск, нуклеація.