

# ФІЗИЧНІ, ХІМІЧНІ ТА ІНШІ ЯВИЩА, НА ОСНОВІ ЯКИХ МОЖУТЬ БУТИ СТВОРЕНІ СЕНСОРИ

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## PHYSICAL, CHEMICAL AND OTHER PHENOMENA, AS THE BASES OF SENSORS

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### THEORETICAL INVESTIGATION OF NANOSYSTEMS USING SIZE QUANTIZATION STARK EFFECT

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#### Abstract

#### THEORETICAL INVESTIGATION OF NANOSYSTEMS USING SIZE QUANTIZATION STARK EFFECT

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Advantages of semiconductor quantum dots for study and diagnostics of biological nanosystems are discussed. A new method for amino acid diagnostics using semiconductor quantum dots is proposed. Interaction of isolated quantum dots with charged amino acids is studied in detail. It is shown that such interaction results in a shift of the quantum dots luminescence spectra by several dozens of meV. This effect provides new possibilities for identification of biological nanoobjects using quantum dots.

**Keywords:** size quantization Stark effect, biological nanosystems, quantum dots, energy shift.

#### Анотація

#### ТЕОРЕТИЧНЕ ВИВЧЕННЯ НАНОСИСТЕМ З ВИКОРИСТАННЯМ КВАНТОВОВИМІРНОГО ЕФЕКТА ШТАРКА

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Обговорюється можливість застосування напівпровідникових квантових точок для вивчення та діагностики біологічних наносистем. Запропоновано новий метод діагностики амінокислот з використанням напівпровідникових квантових точок. Детально вивчається взаємодія квантових точок із зарядженими амінокислотами. Показано, що в результаті такої взаємодії спостерігається зсув спектра люмінесценції квантової точки на декілька меВ. Такий ефект забезпечує нові можливості для ідентифікації біологічних наноб'єктів з допомогою квантових точок.

**Ключові слова:** квантововимірний ефект Штарка, біологічні наносистем, квантові точки, енергетичний зсув.

**Аннотация****ТЕОРЕТИЧЕСКОЕ ИЗУЧЕНИЕ НАНОСИСТЕМ С ИСПОЛЬЗОВАНИЕМ  
КВАНТОВОРАЗМЕРНОГО ЭФФЕКТА ШТАРКА***Сергей И. Покутний, Галина А. Ступаенко*

Обсуждается возможность применения полупроводниковых квантовых точек для изучения и диагностики биологических наносистем. Предложен новый метод диагностики аминокислот с использованием полупроводниковых квантовых точек. Детально изучается взаимодействие квантовых точек с заряженными аминокислотами. Показано, что в результате такого взаимодействия происходит сдвиг спектра люминесценции квантовой точки на несколько мэВ. Этот эффект обеспечивает новые возможности для идентификации биологических нанообъектов с помощью квантовых точек.

**Ключевые слова:** квантоворазмерный эффект Штарка, биологические наносистемы, квантовые точки, энергетический сдвиг.

**1. Introduction**

Semiconductor quantum dots (QDs) are used effectively in opto- and nanoelectronics. For example, IR lasers have been fabricated on the basis of semiconductor QD heterostructures. Such devices have improved characteristics as compared with those of quantum well lasers.

Recently, QDs found new applications in biology and medicine [1]. First of all, QDs are studied as new tools for obtaining an image of living cells and their diagnostics in vivo. As shown elsewhere [2-5], QDs have considerably better properties than fluorescent chromophores which are currently used in biology and medicine, namely: (i) higher quantum yield; (ii) optical activity in the long-wave range of the spectrum; (iii) and significantly greater photochemical stability.

Optical properties of QDs strongly depend on their dimensions. The emission wavelength is increased from  $4 \cdot 10^2$  to  $10^3$  nanometers with increasing the QD radius from 5,0 to 20,0 nm [6-8].

Unlike other fluorescent systems, semiconductor QDs have a threshold excitation energy; i.e., they can be excited by such and greater energies. Thus, the threshold energy must not be equal to the energy of transition within the QDs. Therefore, many QDs can be excited by the light with the same wavelength, whereas each QD emits the light with a different wavelength. Thus, unique spectral properties of QDs are very promising for biological and medicine studies.

In a number of papers (e.g., [3]) a study of multipurpose semiconductor QD samples for detection of cancer cells in living organisms and for creating images of these cells was described. A study of can-

cer cell growth in animals demonstrated that QDs were accumulated in tumors due to both improved transitivity and binding to the biomarker surface of cancer bodies according to the antibody mechanism. High-sensitivity color images of cancer cells have been obtained directly in living organism. Thus, new methods of obtaining high-sensitive images of molecular objects in a living organism using QDs were demonstrated.

Due to their narrow and symmetrical peaks in emitting spectra, semiconductor QDs can be used for optical diagnostics where different colors (wavelengths) and different intensities of the spectral peaks can be used for identification of genes, amino acids, proteins and the molecular chains.

This paper presents a new prospective method of amino acid diagnostics using semiconductor QDs. The main topic is an effect of the amino acid—QD interaction on the emission spectrum of QDs.

**2. Energy Shift of Quantum Dots in the Presence of Amino Acids**

It is known that all 20 amino acids fall into four groups: ones with negative charge; with positive charge; polar and nonpolar. Each amino acid type interacts with QDs in a different way and, thus, differently affects energy levels of charge carriers in QDs and, consequently, the QD emission spectrum. We have carried out detailed microscopic calculation of electron and hole spectra in QDs, which interact with charged amino acids [4, 5].

Let us consider an interaction of QD with charged amino acid (AA). For the sake of simplicity we shall approximate AA with a uniformly charged

sphere. The electrical field on the surface of such sphere is:

$$E = \frac{Q}{\varepsilon_1 R^2} R, \quad (1)$$

where  $R$  is the sphere radius;  $Q$  is the charge, wherein  $Q = (4/3)\pi\rho R^3$  and  $\rho$  is the charge density;  $\varepsilon_1$  is the dielectric constant.

Since the energy gap of QD is less than that of the surrounding material, the charge carrier motion in QD is confined by its volume. Thus, optical properties of QD are determined by the electronic structure of a spatially confined electron-hole pair (exciton) [6-12]. The QD-AA interaction can be considered as effect of the electric field of AA on QD. The case is that under an external electric field a shift of dimensional quantization energy levels for an electron-hole pair in QD in the band-to-band absorption range is determined by the quadratic quantum-dimensional Stark effect [9-12].

As in [9, 10], let us consider a spherical QD with the radius  $a$ , the dielectric constant of QD being  $\varepsilon_2 \gg \varepsilon_1$ . Let us study the effect of the electric field  $E$  on the electron-hole pair spectrum. The electron-hole pair Hamiltonian for QD exposed to the electric field includes, in addition to the kinetic energies of the electron and hole, the following: the energy of the Coulomb interaction of the electron and hole; the energy of the electron and hole interaction with their own images; the energies of interactions with "foreign" images, and the energy of electron and hole interaction with the field. The Hamiltonian can be significantly simplified when  $\varepsilon_2 \gg \varepsilon_1$  [6-8].

We shall consider a case when the QD dimension is confined by the condition:

$$a_h \ll a \leq a_e, \quad (2)$$

where  $a_e = (\varepsilon_2 \hbar^2 / (m_e e^2))$ ;  $a_h = (\varepsilon_2 \hbar^2 / (m_h e^2))$  are Bohr's radii of electron and hole, respectively;  $e$  is the electron charge;  $m_e$  and  $m_h$  are the effective masses of electron and hole, respectively. If condition (2) is satisfied, the polarization interaction provides the main contribution to the potential energy of electron and hole [6-8]. Furthermore, when  $m_e \ll m_h$ , condition (2) allows us to consider the heavy hole motion in the fields with the electron potential averaged over the total electron path (the so called adiabatic approximation).

The electronic structure of an electron-hole pair

within the adiabatic approximation can be easily calculated; see, for example [6-8]. After averaging the potential energy of the electron-hole pair over electron wave functions (in the case of a spherical potential well), we have an expression for the potential energy of a heavy hole moving in the adiabatic potential field of an electron [9, 10]:

$$U(r_h, a, E) = \frac{\hbar^2}{2m_h a_h^2} \left( \frac{a_h}{a} \right) \left[ \frac{1}{1 - (r_h/a)^2} + 2Ci(2\pi n_e) - 2Ci(2\pi n_e (r_h/a)) + \frac{\sin(2\pi n_e (r_h/a))}{2\pi n_e (r_h/a)} + 2 \ln \left( \frac{r_h}{a} \right) + \frac{\varepsilon_2}{\varepsilon_1} - 4 \right] - eEr, \quad (3)$$

where  $n_e$  is the electron principal quantum number;  $r_h$  is the distance between the hole and the center of QD;  $Ci(y)$  is the integral cosine. The last term in (3) results in shifting the potential well bottom for the hole in QD by a value [9, 10]:

$$\Delta x = \frac{(\varepsilon_2 / e)}{(1 + (2/3)\pi^2 n_e^2)} Ea^2 \quad (4)$$

as well as in shifting the dimensional quantization energy levels by a value:

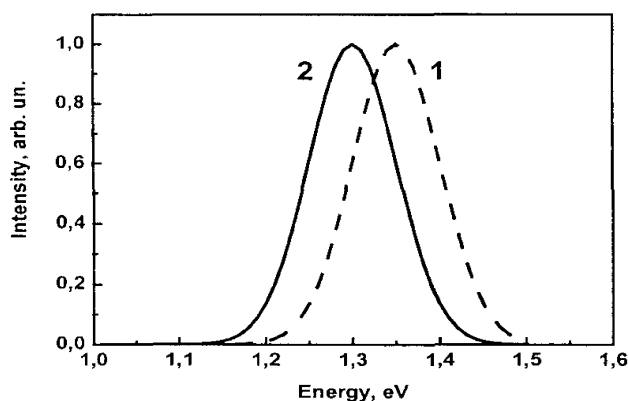
$$\Delta E_h = - \frac{\varepsilon_2}{2[1 + (2/3)\pi^2 n_e^2]} E^2 a^3, \quad (5)$$

where  $\Delta x = (r_h/a)$ .

From (5) it follows that the energy shifts for electron and hole do not depend on the hole principal quantum number  $n_h$  and are determined solely by  $n_e$ . Under the electron field  $E$  the shift of dimensional quantization energy levels  $\Delta E_c$  will be about [9, 10]:

$$\Delta E_c \approx \varepsilon_2 \left( \frac{a_e}{a} \right)^3 E^2 a^3.$$

For the ground electron state  $n_e = 1$  and if  $(a_e/a) \leq (1/3)$ ,  $\Delta E_e \ll \Delta E_h$ . Thus, expression (5) describes the quantum-dimensional quadratic Stark effect, when quantum-dimensional energy levels shift under the electric field by a value proportional to  $E^2 a^3$ . Figure 1 shows an emission spectrum of InAs QD without and with an account for interaction with AA. For calculation, we took the following parameters of InAs:  $a = 5,0 \text{ nm}$ ,  $\varepsilon_2 = 14,9$ ,  $Q = e$ ,  $R = 1,0 \text{ nm}$ ,  $\varepsilon_1 = 1,7$ . The resulting shift of the emission peak was approximately  $\approx 18 \text{ meV}$ .



**Fig. 1.** Emission spectrum of InAs QD without (curve 1) and with an account for interaction (curve 2) with charged AA.

### 3. Conclusions

A case was considered when polarization interaction of an electron and hole with the QD environment contributes mainly to rearrangement of the spectrum. It is shown that when QD interacts with charged amino acids, a shift of dimensional quantization energy levels for an electron-hole pair in QD in the band-to-band absorption range is determined by the quadratic quantum-dimensional Stark effect. An analytical expression for the energy shift for electron and hole levels has been obtained as a function of the electric intensity and QD radius. A case was considered when dielectric constants of QDs and their environment are essentially different. This approach allows us to significantly simplify the expression for the polarized interaction energy of electron and hole with the QD environment.

The energy shift of electron and hole levels de-

fining the shift of the QD luminescence peak has been calculated.

Thus, a good method for using semiconductor QDs for experimental detection of charged amino acid presence with high accuracy is provided.

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