Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2016, т. 14, № 4, сс. 493–501

PACS numbers: 71.35.-y, 71.45.Gm, 73.20.Mf, 73.21.La, 78.67.Bf, 78.67.Hc, 81.07.Ta

New Quasi-Atomic Nanoheterostructures: Superatoms and Excitonic Quasi-Molecules

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In this review, the state-of-the-art of research of artificial atoms (superatoms or quasi-atomic nanoheterostructures) and more complex nanostructures based on them—synthetic molecules is discussed, a new model of an artificial atom, which satisfactorily explains its electronic properties, is proposed, and the prospects for development of the new scientific trend are mentioned.

В цьому огляді обговорюється сучасний стан досліджень штучних атомів (надатомів або квазиатомових наногетероструктур) і більш складних наноструктур на їх основі — синтетичних молекул, запропоновано новий модель штучного атома, що задовільно пояснює його електронні властивості, а також зазначено перспективи для розвитку нового наукового напряму.

В этом обзоре обсуждается современное состояние исследований искусственных атомов (сверхатомов или квазиатомных наногетероструктур) и более сложных наноструктур на их основе — синтетических молекул, предложена новая модель искусственного атома, удовлетворительно объясняющая его электронные свойства, а также указаны перспективы

для развития нового научного направления.

Key words: superatoms, excitonic quasi-molecules, nanoheterostructures, quantum dots, electron, hole, energy spectrum.

Ключові слова: надатоми, екситонні квазимолекули, наногетероструктури, квантові точки, електрон, дірка, енергетичний спектер.

Ключевые слова: сверхатомы, экситонные квазимолекулы, наногетероструктуры, квантовые точки, электрон, дыра, энергетический спектр.

(Received 1 December, 2016)

1. INTRODUCTION

For the development of nanophysics and nanochemistry, the idea of 'artificial atom' (or superatom) [1–4] is fruitful. Superatom (quasi-atomic nanoheterostructures) consists of a core (quantum dots (QDs)) of radius a with dielectric permittivity (DP) ε_2, which is contained in the bulk of the semiconductor (or dielectric) material; core is surrounded by a dielectric (semiconductor) sensor with DP ε_1 [2–9]. The term 'artificial atom' (superatom) is legitimate, given the discrete nature of spectra of the electronic states of superatoms and natural atoms [2–4] as well as the similarity of their chemical activity [9, 10]. Research of quasi-zero-dimensional nanosystems (QN) consisting of nanocrystals of spherical-shape so-called QDs with radii $a = 1–10$ nm, containing within its scope semiconductors (CdS, CdSe, GaAs, Ge, Si, ZnSe) and insulators (Al_2O_3) grown in dielectric (semiconductor) matrices, has received increasing attention due to their unique photoluminescence properties, the ability to emit efficiently the light in the visible or near-infrared bands at room temperature [7–10]. Optical and electro-optical properties of QN (which exhibit the superatomic properties in some cases) largely determines the energy spectrum of space-bounded quasi-particles (electrons, holes, excitons, biexcitons, phonons, polarons, positrons, *etc.*) [2–4, 9, 11].

The heterogeneity (which can be considered as nanoparticles and nanoclusters) arising in heterogeneous structures, due to, in particular, fluctuations in dopant concentration and chemical composition, synthesis conditions in multicomponent systems, plays a special role in nanophysical and nanochemical superatom formation processes [1–4, 9, 11]. Localization of charge carriers over the surfaces of such irregularities under certain conditions leads to the formation of artificial atoms [2–4]. The formation of such superatoms is accompanied by the emergence of the electronic spectra of QN acceptor levels, the nature of which is unknown in most cases,

as well as a sharp drop in the mobility of the charge carriers in QN [5–8].

This review deals with the existing theoretical approaches to the description of artificial atoms and more complex nanostructures based on them—synthetic molecules, the proposed new model of artificial atoms satisfactorily explaining its electronic properties, and the prospects for the development of appropriate new research direction.

2. ARTIFICIAL ATOMS AND EXCITONIC QUASI-MOLECULES IN NANOHETEROSTRUCTURES

In the experimental study of the optical properties of glass samples with the cadmium sulphide and zinc selenide QDs [7], it was found that the electron can be localized on the QD surface, and at the same time, the hole is moving in the QD amount. In [8], the QN consisting of alumina QDs grown in dielectric matrices was studied experimentally. Since the values of band gaps of dielectric matrices (of about 3.3 eV) are smaller than the band gap of alumina QD (of 7.2 eV), there are a possibility of an electron runoff from QD bulk in the matrix and a localization of the electron in the potential well above the QD (a hole moves in the QD bulk). Thus, in [7, 8], apparently for the first time, it was established experimentally an appearance of artificial atoms as nuclei containing the cadmium sulfide, zinc selenide and alumina QDs placed in a dielectric matrix.

In [2–4], it was proposed a new model of an artificial atom (superatom), which is the QN consisting of a spherical QD (core superatom) of radius a, which contains semiconductor (dielectric) with DP ε_2 in its bulk surrounded by a dielectric matrix with DP ε_1 (relative DP $\varepsilon = \varepsilon_1/\varepsilon_2 >> 1$). In the QD bulk, the hole h moves with the effective mass m_h, and electron e with the effective mass $m_e^{(1)}$ is in a dielectric matrix. In such QN, lowest electronic level is located in the matrix, and the most humble level of the hole is in the QD amount. Large shift of the valence band (of about 700 meV) is the localization of holes in the QD bulk. Large shift of the conduction band (of about 400 meV) is a potential barrier for electrons (electrons move in the matrix and do not penetrate the QD bulk). Energy of the Coulomb electron–hole interaction as well as energy of the polarization of electron interaction with the QD–matrix interface (as the QD DP ε_2 is far superior to the matrix DP ε_1) cause the localization of the electron in the potential well above the QD [2–4].

In [2–4], in the framework of the modified method of the effective mass [10], it was developed a theory of superatom of spatially separated electrons and holes (the hole is in the QD amount, and the electron is localized on the spherical surface QD–matrix interface).

As a core, QD protects semiconductors and dielectrics containing in its bulk. Energy spectrum of superatom, starting with the value of the QD critical radius $a \geq a_c^{(1)}$ (of about 4 nm), will be consisting entirely of discrete quantum levels. This is called hydrogen-superatom [2–4]. A valence QD is localized above the surface of the electron. Quantum-discrete energy levels of superatom are located in the (dielectric or semiconductor) matrix band gap. Electrons in superatom linked to well-defined atomic orbitals are localized in the vicinity of the nucleus (QD) [2–4]. Ionization energy of superatoms take large values (of about 3 eV), which is almost three orders of magnitude higher than the binding energy of excitons in semiconductors [2–4].

As the QD radius a increases so that $a >> a_{ex}^0$, (where

$$a_{ex}^0 = \frac{2\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2} \frac{\hbar}{\mu_0 e^2} \tag{1}$$

is two-dimensional electron Bohr radius ($\mu_0 = m_e^{(1)} m_h/(m_e^{(1)} + m_h)$—the reduced mass of the electron–hole pairs of spatially separated electrons and holes), spherical QD–matrix interface transforms into a flat interface. In this artificial atom, electron is localized on the QD–matrix surface becomes two-dimensional ($2D$) [2–4]. In the potential energy in the Hamiltonian describing the motion of an electron in a superatom, the main contribution in this case brings the energy of the Coulomb interaction of electron with a hole [2–4]:

$$V_{eh}(r) = -\frac{1}{2}\left(\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2}\right)\frac{e^2}{r} \tag{2}$$

(where r—the distance of the electron from the QD centre). Polarization interaction energy of both electron and hole with a spherical surface QD–matrix interface gives a much smaller contribution to the potential energy in the Hamiltonian. In a first approximation, this contribution can be neglected [2–4]. The energy spectrum of two-dimensional electrons in an artificial atom takes the Coulomb form [2–4]:

$$E_n = -\frac{Ry_{ex}^0}{(n + 1/2)^2}, \quad Ry_{ex}^0 = \frac{(\varepsilon_1 + \varepsilon_2)^2}{4\varepsilon_1^2\varepsilon_2^2}\left(\frac{\mu_0}{m_0}\right) Ry_0, \tag{3}$$

where n (= 0, 1, 2)—the principal quantum number of the electron, $Ry_0 = 13.606$ eV—the Rydberg constant. The binding energy of the ground state of the two-dimensional electron, according to (3), is given by:

$$E_{ex}^0 = -4Ry_{ex}^0. \tag{4}$$

With the binding energy (4) of the ground state of the electron, it means the energy required for the decay of the bound state of an electron and a hole (in the state with $n = 0$) in a superatom.

From the dependence of the binding energy $E_{ex}(a,\varepsilon)$ of the ground state of an electron in a superatom (obtained in [4] by the variational method) containing ZnSe QDs of radius a, it follows that the bound state of an electron occurs near the spherical surface QD–matrix interface, starting with the critical QD radius: $a \geq a_c^{(1)} = 3.84$ nm. While hole is moving in a QD bulk, the electron is localized on the surface of the spherical QD–matrix interface. In this case, the energy of the Coulomb interaction $V_{eh}(r)$ (2) between the electron and the hole as well as the energy of the polarization interaction of an electron and a hole with a spherical surface QD–matrix interface prevail over the energy of size quantization of electron and hole in the artificial atom. Thus, it was found in [4] that the occurrence of superatom has a threshold, and it is possible only with QD radius $a \geq a_c^{(1)} = 3.84$ nm.

With the growth of the QD radius a, it is scanned an increase in the binding energy of the ground state of an electron in a superatom. In the range of radii, $4.0 \text{ nm} \leq a \leq 29.8$ nm, binding energy of the ground state of an electron in a superatom significantly exceeds (by 4.1–76.2 times) the value of the exciton binding energy $\bar{E}_{ex}^0 \approx 21.07$ meV in the zinc selenide single crystal [4]. Beginning with the QD radius $a \geq a_c^{(2)} = 29.8$ nm, the binding energy of the ground state of an electron in a superatom asymptotically follow the value $E_{ex}^0 = -1.5296$ eV characterizing the binding energy of the ground state of two-dimensional electrons in an artificial atom (4) [4].

The effect of a significant increase in the binding energy of the ground state of an electron in a superatom is mainly determined by two factors [2–4]: 1) a significant increase in the Coulomb electron–hole interaction energy $|V_{eh}(r)|$ (2) ('dielectric enhancement'); 2) a spatial limitation on the quantization QD volume, while with increasing QD radius a, since the QD radius $a \geq a_c^{(2)} = 52a^0{}_{ex} = 29.8$ nm, superatom becomes two-dimensional with the binding energy of the ground state E_{ex}^0 (4), the value of which is greater by almost two orders of magnitude than the exciton binding energy in the zinc selenide single crystal. The effect of 'dielectric enhancement' due to the fact that, when the matrix DP ε_1 is significantly less than the QD DP ε_2, an important role in the interaction between the electron and the hole in the superatom is playing by field created by these quasi-particles in the matrix. At the same time, the interaction between the electron and the hole in the superatom is much greater than in a semiconductor with DP ε_2 [2–4].

The optical properties of borosilicate glass samples containing zinc selenide QD were studied in [7]. According to X-ray diffraction

measurements, the mean radii $\bar{a}$ of ZnSe QD are ranged as $\bar{a} \approx 2.0$–4.8 nm. At low concentrations of QDs ($x = 0.003\%$), their interaction can be neglected. The optical properties of such QN are mainly determined by the energy spectrum of electrons and holes localized near the surface of spherical single QDs grown in the glass matrix. A maximum (peak) of the spectrum of low-temperature luminescence was found in [7] as $\bar{E} = 2.66$ eV at $T = 4.5$ K that is below the ceiling of the band gap ($E_g = 2.823$ eV) of a zinc selenide single crystal. The $\bar{E}$ peak shift in low-temperature photoluminescence spectrum with respect to the ZnSe single crystal band gap in the short wavelength region is equal $\Delta\bar{E} = \bar{E} \quad E_g = -165$ meV. Comparing the energy of the ground state of the electron ($E_0(a,\varepsilon) - E_g$) in the artificial atom with the value of the peak of the luminescence spectrum $\Delta\bar{E} = -165$ meV, the average radius $\bar{a}_0 \cong 4.22$ nm for zinc selenide QDs was obtained in [4] that is in the range of the mean radii ($\bar{a} \approx 2.0$–4.8 nm) for QDs studied under experimental conditions [7]. Thus, the proposed model of superatom allows to interpret the mechanism of occurrence of the peak of the luminescence spectrum $\Delta\bar{E} = -165$ meV for nanosystems studied experimentally in [7].

The distance between two (or more) of artificial atoms up to a certain critical value D_c between the QD surface (*e.g.*, a smaller value of the two Bohr radii of the electron in a superatom) will result in an overlap of the outer electron orbitals in a superatom and the emergence of the exchange interactions and, therefore, more powerful type of bond [2–4] (compared with ties to the natural molecules). As a result, conditions can be created for the emergence of artificial atoms as new quantum nanosystems—quasi-molecules or artificial molecules [2–4, 9, 11].

Specified type of bond is new, even because, despite the nature of the exchange, it can be realized at wavelengths much longer than the characteristic lengths for known natural molecules. Indeed, the value of the overlapping integral of the outer electron wave functions in the quasi-molecule is essential over distances far exceeding the characteristic length for the known natural molecule [3, 9, 11]. This enhancement effect in the exciton quasi-molecule binding energy is because the main contribution to the binding energy makes the exchange interaction energy of electrons, the renormalized Coulomb and polarization interactions of spatially separated electrons and holes [3, 9, 11]. The exciton quasi-molecule QN occurs starting from a distance $D \geq D_c^{(1)} \cong 2{,}1$ nm between the surfaces of QDs [3, 9, 11]. The formation of such quasi-molecule has a threshold and is only possible in the QN comprising QDs with average radii of $\bar{a}_1$, in which the distance D between the surfaces of QD exceeds some critical distance $D_c^{(1)}$ [3, 9, 11].

The binding energy of superatom is $E_{ex}(\bar{a}) \cong -98$ meV [2–4]. The

energy of the singlet ground state of the quasi-molecule exciton (5) takes the value $E_0(\tilde{D}_1, \bar{a}_1) \approx -202.84$ meV [11]. It should be emphasized that we used the criterion of applicability of the variational calculation of the binding energy $E_B(\tilde{D}, \tilde{a})$ for quasi-molecule, which was carried out (the ratio $E_b^{(1)}(D_1, \bar{a}_1) / E_{ex}(\bar{a}_1) \cong 0,07$).

With the increase of the distance D between the surfaces of QD, starting with the value $D \geq D_c^{(2)} = 4.4$ nm, QN quasi-molecule exciton splits into two superatoms (see Fig. 1 in [3, 9, 11]). Thus, QN quasi-molecule may occur if there are conditions $D_c^{(1)} \leq D \leq D_c^{(2)}$. In addition, quasi-molecule can exist only at temperatures below a certain critical temperature T_c 79 K. Biexciton (quasi-molecule exciton) arises in single-crystalline CdS with a binding energy $E_b = 0.59$ meV (at temperature of 6.84 K). E_b exceeds the binding energy $E_b^{(1)}$ of the quasi-molecule in nanosystems by more than an order of magnitude [3, 9, 11]. In the binding energy of the quasi-molecule, as follows from the results of variational calculations [3, 9, 11], the main contribution to the exchange interaction energy of electrons and holes, which is substantially greater than that of energy of the Coulomb interaction between electrons and holes (with the ratio of ≤ 0.11). The calculations of the binding energy of the ground state quasi-molecule in the QN are variational, so they can give low values for the binding energies $\left|E_B(\tilde{D}, \tilde{a})\right|$ and $\left|E_b^{(1)}\right|$. Thus, the observed effect is a significant increase in the binding energy of the singlet ground state of the exciton quasi-molecule (of spatially separated electrons and holes) in the QN (more than an order of magnitude) than the binding energy of the biexciton in a cadmium sulphide single crystal [3, 9, 11].

This effect is a significant increase in the binding energy of the singlet ground state of the exciton quasi-molecule due to the fact that, due to the presence of the QN interface (QD–matrix), the energy of the exchange interaction between electrons and holes (the renormalized Coulomb interaction (2) of spatially separated electrons and holes) in the QN will be much greater than the energy of the exchange interaction between electrons and holes in a single crystal [3, 9, 11].

It should be noted that, in the experimental work [7], apparently, it was firstly discovered the interaction of the charge carriers localized on the cadmium sulphide QD surface. At the same time, we have proposed a quasi-molecule model [3, 9, 11] allowing interpreting the mechanism of occurrence of the peak of the absorption spectrum of nanosystems studied in [7].

In a single atom of an alkali metal, valence electron is moving in the Coulomb field of the atomic core having the same functional dependence on r as the Coulomb field (2), in which the valence electron in a hydrogen-like model of artificial atom [2] is moving. This

leads to the fact that the energy spectra of the valence electron in a single atom of an alkali metal and an artificial atom (3) describe the hydrogen-type spectrum [2]. At the same time, the number of possible quantum states of the valence electron in the model of artificial hydrogen-type atom is the same as the number of quantum discrete states of the valence electron in a single atom of an alkali metal [2]. In [2], the positions of the energy levels of the valence electron in the individual atoms of alkali metals (K, Rb, Sc) and the new artificial atom X are similar (as well as the level shifts of the valence electron, $\Delta E_{\mathrm{Rb}}^{\mathrm{K}}, \Delta E_{\mathrm{Sc}}^{\mathrm{Rb}}, \Delta E_{X}^{\mathrm{Sc}}$, relative to the adjacent level). In [2], it was assumed that the shift of the energy level E_X of artificial atom X (with respect to the energy level E_{Sc} of the Sc atom) will be the same as the shift of the energy levels E_{Rb} of the Rb atom (relative to the energy level E_{Sc} of the Sc atom) (*i.e.*, $\Delta E_{X}^{\mathrm{Sc}} = \Delta E_{\mathrm{Sc}}^{\mathrm{Rb}}$). Then, the level of the valence electron in artificial atom takes a value $E_X = -593$ meV. Using the dependence of the binding energy $E_{ex}(a,\varepsilon)$ of the ground state of an electron in an artificial atom, obtained in [2] by the variational method, containing zinc selenide QD with radius a, in [2], it was found the radius of zinc selenide QD $a_1 = 5{,}4$ nm, which corresponds to the level $E_X = -593$ meV. It should be noted that the energy levels of a valence electron in the individual atoms of alkali metals (K, Rb, Sc) and the new artificial atom X is in the infrared spectral region [2]. Thus, we proposed in [2] a new model of an artificial atom allowing to offer and calculate a new nanoheterostructure quantum dot—artificial atom X, the natural analogue of the group of alkali metals following the caesium and absent in the periodic (Mendeleev) table.

3. FUTURE STUDIES OF ARTIFICIAL ATOMS AND EXCITONIC QUASI-MOLECULES

These results suggest the possibility in principle for creating a plurality of artificial atoms, including natural analogues, with new physical and chemical properties [2–4]. Based on that, we can construct new quantum nanosystems—quasi-molecules and quasicrystals. Governing their symmetry and lattice period will allow to realize the unique physical and chemical effects and phenomena, to create new principles in materials science [2–4, 9, 11].

The observed effect is a significant increase in the binding energy of an electron in a hydrogen-type superatom [2–4] (by almost two orders of magnitude greater than in closed nanosystems, in which electrons and holes are localized in the QD bulk) can afford to use them as an active medium for a new generation of nanolasers emitting in the optical spectrum as well as a base element of a new generation of optical nanocomputers.

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