The deformation effects in isovalent doping of CdSe quantum dots with a multilayer shell for their biomedical applications

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TOPICALITY and AIMS. The modern nanotechnologies make it possible to use new materials and methods in biology and medicine. Among such materials are semiconductor heterostructures with quantum dots (QD), which have a high quantum yield of photoluminescence, the energy of the emitted quantum, which depends on the size of the crystal, and are able to retain their optical properties for a long time. This is what makes them extremely attractive for widespread use in medicine. The exclusive properties of the structures with QDs reveal themselves only in the case where the QDs are uniform enough by their shapes and dimensions. Therefore, the main task at the QD growing is the control over their morphology: the average size, density, uniformity. Isovalent impurity is not an electrically active impurity, i.e. it does not increase the charge carrier concentration. However, it substantially changes the conditions of QD formation owing to the induced diffusion-deformation flux. The investigation of deformation effects in QD with a multicomponent shell doped with an isovalent impurity is an urgent task associated with their use in medicine.

THE MODEL

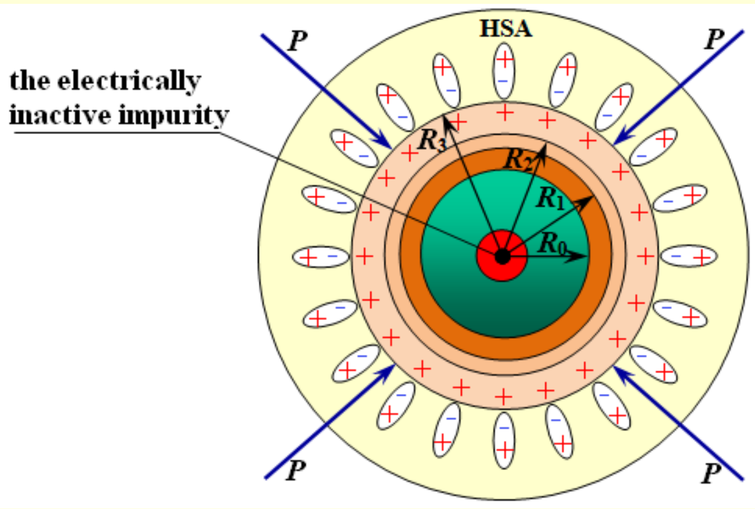

Fig. 1. The model of an isovalently doped the core / multilayer shell quantum dot that interacts with albumin molecules

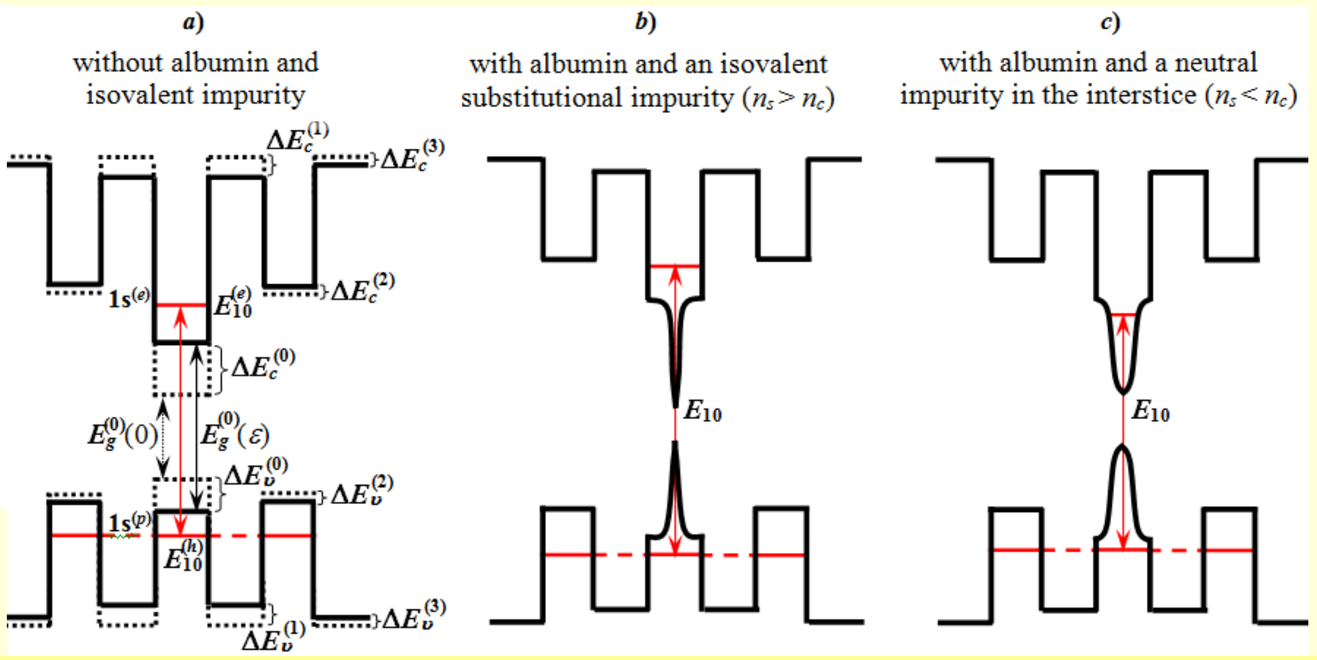

Fig. 2. The band scheme of the CdSe-core / ZnS/CdS/ZnS-shell quantum dot (solid line) and the band scheme of the correspon-ding bulk materials (dotted line) in the absence of an isovalent impurity and HSA (a) and in the presence of an isovalent impurity and HSA (b, c)

Due to the self-consistent redistribution of the electric charge density in the QD, there is a non-uniform electric field *E* on its surface. As a result of the interaction (attraction) of the dipole molecule of HSA with this electric field, on the QD surface there is the pressure that can be determined by the formula:

$$P = \frac{n_s}{1 + n_s S_A} p \frac{dE}{dr}\Big|_{r=R_3}, \qquad (1)$$

where n_s p and S_A are surface concentration, the dipole moment and the effective cross section of the HSA molecule, R_3 is the radius of the outer layer of shell.

Pressure leads to shift the edges of the allowed bands, thereby changing the energy spectrum of electrons and holes and the width of the band gap. The energy displacements of the edges of the permitted bands under the influence of elastic deformations:

$$\Delta E_c^{(i)} = a_c^{(i)} \varepsilon^{(i)}, \qquad \Delta E_v^{(i)} = a_v^{(i)} \varepsilon^{(i)}, \qquad (2)$$

where $a_c^{(i)}, a_v^{(i)}$ are the constants of hydrostatic deformation potential of the conduction band and valence band,

$$\varepsilon^{(i)} = \varepsilon_{rr}^{(i)} + \varepsilon_{\theta\theta}^{(i)} + \varepsilon_{\varphi\varphi}^{(i)} \qquad i = 0 \equiv \text{CdSe}, \quad 1 \equiv \text{ZnS}, \quad 2 \equiv \text{CdS}, \quad 3 \equiv \text{ZnS}$$

To determine the components of the deformation tensor, it is necessary to find the displacements of atoms in the materials of the QD core (i = 0) and layers of shell (i = 1, 2, …, n). To do this, we will write down the equation of equilibrium (3):

$$\vec{\nabla} \operatorname{div} \vec{u} = -D_1 \cdot \vec{F}^{(1)}(\vec{r}), \qquad (3) \qquad \vec{F}^{(1)} = \frac{2\Delta\Omega}{3\pi^{3/2}} \left(C_{11}^{(1)} + 2C_{12}^{(1)}\right) \frac{1}{r_0^5} r e^{-\frac{r^2}{r_0^2}} \vec{n}$$

where $\vec{F}^{(1)}$ is the volumetric force produced by the impurity in the QD; $\Delta\Omega$ is the change in the volume of the QD material due to the embedded isovalent impurity; r_0 is the effective radius of the impurity atom; $C_{11}^{(i)}$ and $C_{12}^{(i)}$ are the elastic constants of these materials;

1) for impurity of substitution: $\Delta\Omega = 4\pi(r_i^3 - r_{Se}^3)/3$ 2) for atom in the internode: $\Delta\Omega = 4\pi r_a^3/3$

where r_{Se}, r_a are the Se^{2+} ion radius and the radius of the impurity atom.

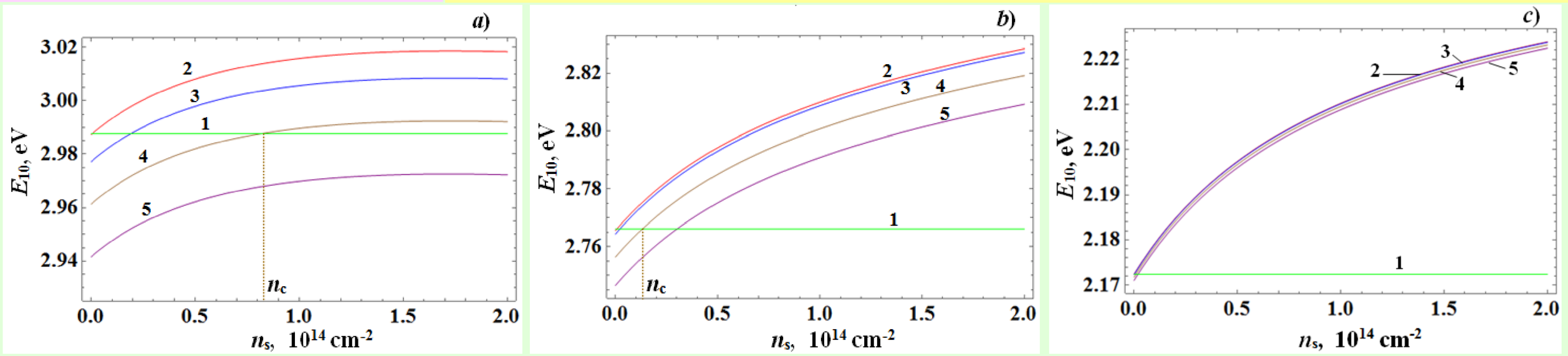

Fig. 3. The dependence of the width of the optical band gap on the value of the HSA surface concentration in CdSe-core / ZnS/CdS/ZnS-shell quantum dot at different values of the QD core radius (R_0 = 2 *nm* (a); R_0 = 2.5 *nm* (b); R_0 = 6 *nm* (c)) and at different impurities: without impurity and without HSA (line 1); without impurity (line 2); with an isovalent substitution impurity (line 3); with an interstitial Cr atom (line 4); with an interstitial Te atom (line 5)

CONCLUSIONS

Based on the method of self-consistent electron-deformation coupling, the deformation effects in the CdSe-core / ZnS/CdS/ZnS-shell quantum dot doped with an electrically inactive impurity, which interact with human serum albumin, were investigated. The pressure on the quantum dot surface, which arises due to the electrostatic attraction of human serum albumin molecules, is calculated, depending on the geometric sizes of quantum dot, the average electron concentration and the albumin concentration, for different types of impurities (substitutional impurities or interstitial impurities). The regularities of change of deformation and band structure of the bionanocomplex of multilayer shell quantum dot with human serum albumin at change of geometrical sizes and structure of quantum dot and surface concentration of human serum albumin are established. It is shown that, depending on the type of impurity and the concentration of HSA, the width of the optical band gap can be smaller or larger compared to the same value for the undoped QD and without HSA. The established regularities can be the basis for the development of bionanosensors for the determination of albumin concentration based on CdSe semiconductor QDs with a ZnS/CdS/ZnS multi-layer shell and allow to determine the location of the impurity.