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Electron transport in single colloidal quantum dots in an interelectrode nanogap

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Based on the current-voltage characteristics of single colloidal QDs -InSb, -PbS, -HgSe, -CdSe quantum dots, on random samples statistically determined and investigated the mechanisms of barrier and ballistic tunneling, Coulomb confinement, quasi-periodic modulation of electron transport in the model of a deep extended potential well and depending on QDs size and de Broglie wavelength for the electron. The possibility of manifestation of Bloch oscillations has been experimentally confirmed. The parameters of all investigated processes were determined and tabulated.

Keywords: Nanoparticle, quantum dot, dimensional quantization, quantum selection, barrier and ballistic tunneling, Coulomb confinement, Coulomb ladder, Bloch oscillations.

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Properties of the electron transport in quantum-size particle (QP) are their major characteristic, and studying of its mechanisms is of big scientific and practical importance. A detailed investigation is carried out of the mechanism of tunnel jump over a single ultra-small ($\sim 1\,\text{nm}$) QP that takes place under the energy condition required for such a jump [1]. A model of single-electron transport in QP as a large atom is investigated [2]. A number of works, for example [3–5], investigated the electron transport for the cases of a complex configuration composed of several interrelated QPs. In contrast to the above-mentioned cases, interesting is the case of large (up to $10\,\text{nm}$) quantum-size particle as a deep extended potential well with an electron inside moving in conditions of size quantization and resonance state. A detailed theoretical consideration of all possible variants of electron transport through a nanoparticle is carried out in [6]. There are extremely few experimental investigations in this field, which may be caused by technological difficulties of producing quantum-size particles.

In this work we experimentally studied and explained properties of the electron transport using single quantum-sized nanoparticles of the most interesting semiconductors synthesized by us: InSb, PbS, HgSe, CdSe. The specimens were synthesized using technologies described in a number of our works, with selection of required conditions for different variants of composition [7,8]. Each lot of specimens was controlled on a random sample of QPs by methods of scanning electron microscopy used to control stoichiometric composition and transmission electron microscopy (TEM) used to control geometry and sizes. QP samples were selected for the measurements as polygonal nanocrystals with minimum dispersion of dimensions.

The study was carried out on the basis of current-voltage curves (CVC) measured at room temperatures by the method of scanning probe microscopy developed and described in our works [9,10]. Immediately before the measurements the nanoparticles were made free from ligands by sediment detachment through centrifugation and redispersion in hexane and set out as an island monolayer on a conducting substrate using the technology of the Langmuir–Blodgett film (LBF) [11]. Fig. 1 shows TEM-images of QP sample fragments in a LBF-matrix. In each specimen at least 20 points-particles of random samples were measured. For each of four types of specimens a total of at least 200 points-particles were measured.

The main experimental and calculated data, as well as parameters of semiconductors are represented in the table: E_g — energy gap width, m — effective mass, m_0 — free-electron mass [12].

Fig. 2 shows typical CVCs having three variants of curve shape in each of four groups: without singularities (curves *1*, *1'*); with poor singularities (curves *2*, *2'*) and with definite singularities (curves *3*, *3'*). In this case statistical fractions p of QP number with definite singularities of CVC were distributed as shown in the table.

CVCs of nanoparticles without singularities, as shown in a number of our works [10,13], are defined by mechanisms of electron tunneling through potential barrier (the barrier tunneling) ($I \sim \exp[\alpha V]$) and Coulomb current limitation by space charge ($I \sim V^{\beta}$). Fig. 3, *a*, *b* shows an example of CVCs for QP-InSb that make it possible to conclude that in the interval of low voltages V current I is limited by the limitations of Coulomb' law, and in the interval of high voltages it is limited by tunneling. The same regularities were observed for other variants. The table shows statistically average values determined for α and β

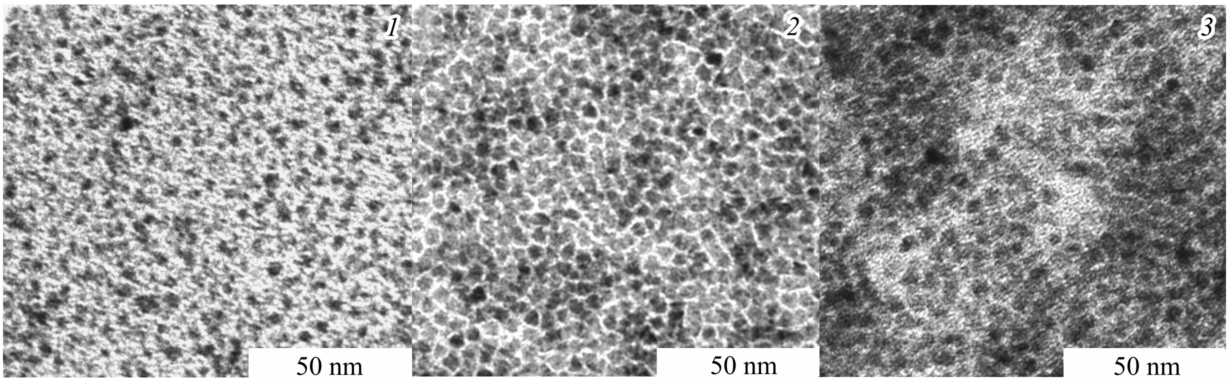

Figure 1. TEM-images of LBF-monolayers of QP-CdSe (*1*), QP-InSb (*2*), QP-PbS (*3*).

Summary

Semi-conductor	E_g, eV	m/m_0	α	β	a, nm	$\tilde{E}_1$, eV	$\tilde{E}_2$, eV	$\tilde{E}_{exp}$, eV	n	Λ_1, nm	Λ_2, nm	p, %	$\sim \Delta\tilde{E}$, eV	$\sim \Delta\tilde{E}_{exp}$, eV	γ
InSb	0.23	0.014	1.4	2.4	2−4	2.5	10	3.2	1	5.3	2.7	70	0.3	0.3	1.18
PbS	0.41	0.08	3.4	3.6	2−5	0.35	1.4	1.2	2	5.6	2.8	50	0.15	0.15	1.38
HgSe	~ 0.1	0.045	1.8	1.5	3−7	0.2	0.8	0.9	2	5.3	2.6	45	0.1	0.1	1.72
CdSe	1.74	0.13	2.7	1.1	3−5	0.15	0.6	0.7	2	8.0	3.5	30	0.1	0.1	1.94

parameters, that make it possible to conclude that from the QP-CdSe specimen to the QP-InSb specimen α decreases due to decrease in the effective electron mass, while β increases due to increase in their mobility. An exception is the QP-PbS, which are characterized by a string impact of polarization effects due to high values of dielectric constant.

The size quantization properties in QP are defined by processes of electron motion in it described by the Schrodinger's equation. Solution to the equation exists only for a countable set of energy values $\tilde{E}_n$ and is a set of wave functions countable by quantum numbers n that form a general solution as an additive superposition of particular solutions [6]. For the case of one-dimensional linear motion in a deep rectangular potential well with a width of a the solution to the Schrodinger's equation with respect to eigenfunctions $\tilde{E}_n$ and formula for the de Broglie wavelength Λ can be obtained in the following form [6]: $\tilde{E}_n \sim h^2 n^2 (8ma^2)^{-1}$; $\Lambda \sim h(2m\tilde{E}_n)^{-1/2}$ (h — Plank's constant).

In a QP, as a deep elongated potential well, a selection of electron steady states takes place. Any affecting energy impact on an electron in the QP results in its transition from one steady state to another. The stability of state of an electron moving in a deep elongated potential well and the shape of its standing wave function may mean that its motion between the QP boundaries has a quasiperiodic resonance character. The most important specifics of motion of an electron injected into QP is the manifestation of quasiperiodic oscillations of the transmission coefficient with changes in the electron energy [6]. In our case it is manifested as pulsations of current. It can be interpreted physically as a result of interference of the de Broglie waves reflected from potential jumps at the boundary of the potential well.

The crystalline structure, expressed in the polygonal shape of the nanocrystal, and the size of QP are critical for all processes of size quantization. In our case all nanocrystals, except for QP-CdSe, have cubic crystal system, and we can presumably consider the most simple variant of resonance motion of the electron — between parallel planes of a right parallelepiped with maximum distance between them equal to one of dimensions of the QP. Actually, the results of CVC measurements will be dependent on the positioning of the QP monocrystal between electrodes in the nanogap in relation to field lines. Direct measurements of dimensions by TEM method for the selected lots of samples allowed us to obtain information on dispersions of a dimensions (see the table).

For values of a energies were calculated in resonance states $n = 1$ ($\tilde{E}_1$) and $n = 2$ ($\tilde{E}_2$) (see the table) by the following formula: $\tilde{E}_n \sim h^2 n^2 (8ma^2)^{-1} \sim 0.3n^2(a^2 m/m_0)^{-1}$. The calculated values can be compared with the voltages in the points of CVC singularities — $\tilde{E}_{exp}$ (see the table). The table also shows de Broglie wavelengths for electron calculated by the following formula: $\Lambda \sim h(2m\tilde{E}_n)^{-1/2} \sim 1.2(\tilde{E}_n m/m_0)^{-1/2}$. In the process of all calculations a and Λ are expressed in nanometers, $\tilde{E}_n$ — in electron-volts.

The degree of manifestation of the size quantization in QP depends on the ratio between a and Λ. With $a > \Lambda$ it does not manifest and the CVC has almost no nonlinear distortions (curves *1*, *1'* in Fig. 2). With $a \sim \Lambda$ the

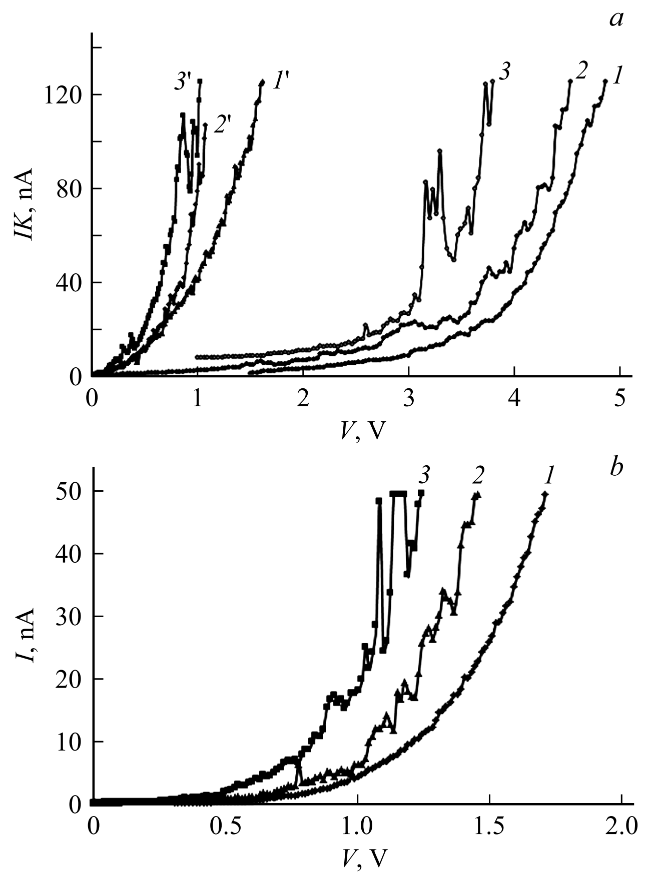

Figure 2. Current-voltage curves of quantum-sized particles. a — QP-InSb (transition coefficient $K = 1$) (*1–3*) and QP-HgSe ($K = 2.5$) (*1'–3'*); b — QP-PbS (*1–3*).

size quantization is poorly manifested, the CVC follows the shape of the previous case, but is characterized by quasiperiodic nonlinear distortions (curves *2*, *2'* in Fig. 2). With $a < \Lambda$ the size quantization is severely manifested, the CVC in the figures has the shape of curves *3*, *3'*. In this case, the lower is dispersion of a dimensions in relation to Λ, the greater is the fraction of p curves with singularity. With increase in the manifestation of size quantization a significant increase in current is observed (curves are shifted left in Fig. 2), which can be explained by competitive predominance of the size quantization and resonance motion over the mechanisms of barrier tunneling and Coulomb current limitation by space charge.

In case of finite motion of electron in QP Bloch oscillations are theoretically possible [14]. However, in this case, the main obstacle for them is their short life time caused by the electron scattering on defects of the crystal lattice and phonons. In a quantum-size particle with dimensions of $a \sim \Lambda$ the electron moves in a ballistic and, perhaps, resonant manner, as if it „does not respond" to the structural interference, and the path of its motion in a three-dimensional QP „is selected" by quantum selection of impulse in the Brillouin zone. These circumstances may be indicative of a real possibility of Bloch oscillations acting in the QP in the case of current flow or any other energy impacts on the electron. This can explain the behavior of such CVCs as curves *2* in Fig. 2 with a character similar to the Coulomb staircase. The energy step $\Delta V \sim \Delta\tilde{E}$ of this oscillation in CVCs can be calculated by differentiating the formula for the energy of electron as a function of $\tilde{E}(a)$: $\Delta\tilde{E} \sim 0.6a^3(m/m_0)^{-1}\Delta a$. By assuming Δa equal to the lattice spacing of the QP nanocrystal, approximate values of $\Delta\tilde{E}$ can be calculated and compared with the data obtained from curves *2* in Fig. 2 — $\Delta\tilde{E}_{exp}$ (see the table).

With applied voltage V from zero and above, the electron injected from the electrode to the QP is transferred to a steady resonant state of $n = 1$. The first zone of singularity $V_1 \sim \tilde{E}_1$ is manifested on the CVC. With further increase in V the electron is removed from this state by tunneling through the boundary and creating current until some next electron is transferred to the steady resonant state of $n = 2$. In this case, the second zone of singularity $V_2 \sim \tilde{E}_2$ is manifested on the CVC. CVC of the transition gap is defined by the ballistic tunneling of electrons that are successively flowing through the QP as a rectangular potential barrier. The probability of this tunneling can be calculated as follows [15]:

$$\exp[-a[8m(\tilde{E} - V)]^{1/2}/h] \sim \exp[-\gamma(n^2 - 3Va^2m/m_0)^{1/2}].$$

Here $\gamma > 1$, an artificially introduced parameter, takes into account the decrease in the probability of electron tunneling due to deviation of its wave vector from the electric field line depending on the electron velocity (energy) : the higher is the energy $\tilde{E}_{1,2}$, the lower is γ, that follows from the table as well.

Fig. 3,c shows CVCs plotted in accordance with the following formula: $I \propto \exp[-\gamma(n^2 - 3Va^2m/m_0)^{1/2}]$ or $I \sim I_0\exp[-\gamma C]$, while the table shows values of γ. Here we have introduced C, a dimensionless parameter depending on voltage.

Thus, the electron transport in single colloidal quantum-sized particles of InSb, PbS, HgSe, CdSe semiconductors is defined by the character of current-voltage curves having three variants depending on the ratio between the particle size and de Broglie wavelength for the electron: 1) smooth monotone curve caused by mechanisms of barrier tunneling and Coulomb limitation; 2) quasiperiodic modulated curve similar to the Coulomb staircase; 3) curve with clearly manifested singularities in the form of sharp oscillations of current in some voltage ranges defined by the energies of quantum selection. Observed singularities are defined by the mechanism of size quantization and the state of periodically-oscillating resonance of the electron motion between QP boundaries, while the quasiperiodic modulation can be explained by the model of Bloch oscillations. In this work the parameters that characterize the observed phenomena and properties are determined and represented in a tabular form.

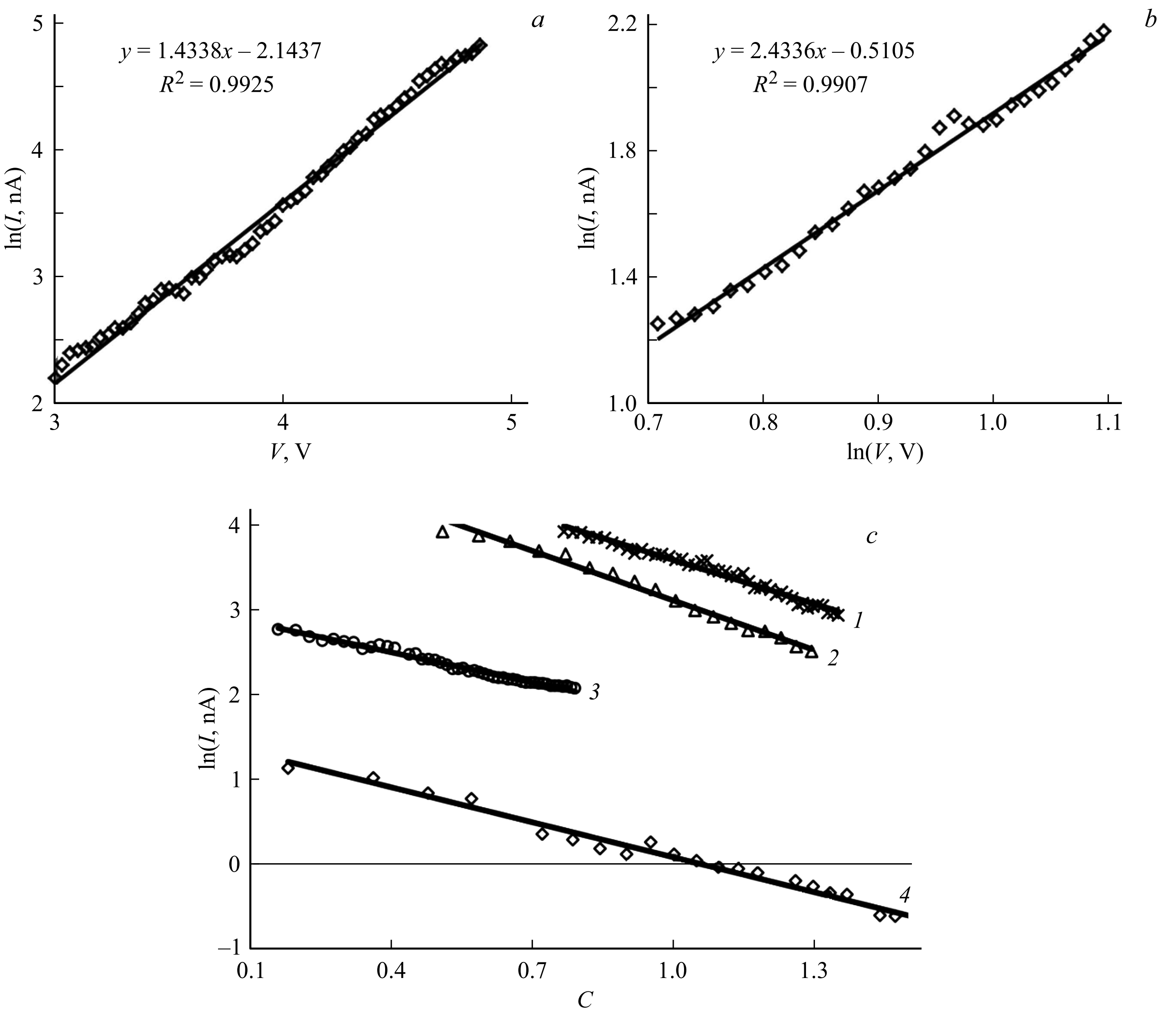

Figure 3. Current-voltage curves of QP-InSb in coordinates of formulae of tunneling (*a*) and Coulomb limitation (*b*). *c* — curves $\ln I \sim C = (n^2 - 3Va^2m/m_0)^{1/2}$: *1* — QP-HgSe, $a = 4\,\text{nm}$, $n = 2$; *2* — QP-CdSe, $a = 4\,\text{nm}$, $n = 2$; *3* — QP-InSb, $a = 3\,\text{nm}$, $n = 1$; *4* — QP-PbS, $a = 5.5\,\text{nm}$, $n = 2$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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