UDC 621.315.5.001:53 DOI: 10.15407/Surface.2024.16.037

OPTICAL SPECTROSCOPY OF CADMIUM SULFIDE NANOCRYSTALS IN THE ULTRAVIOLET SPECTRUM

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In this mini-review, theoretical studies of some optical properties of cadmium sulfide nanocrystals in the ultraviolet spectrum are considered. A variational method was described by which the energy of the ground state of the electron-hole pair was obtained as a function of the radius of the cadmium sulfide nanocrystal within the effective mass approximation. A mechanism is proposed that describes the absorption of the considered nanosystem in the ultraviolet spectral ranges. It is shown that the absorption peaks of the nanosystem are caused by interband electron transitions from the energy quantum-confined level lying in the valence band of the CdS NC to the energy quantum-confined level located in the conduction band of the cadmium sulfide NC. It has been established that the formation of the energy quantum-confined levels of an electron and a hole in a CdS nanocrystal, is significantly affected by the energy of the Coulomb electron-hole interaction, as well as the energy of the polarization interactions of the electron and hole with the interface (nanocrystal – matrix).

Keywords: *electron transitions, electron quantum-confined states, coulomb electron-hole interaction.*

INTRODUCTION

Semiconductor nanocrystals (NCs), or quantum dots, which are characterized by a size smaller than 3 nm, are still intensively studied [1 – 6]. The importance of these is due to the fact that in these nanosystems, wide ranges of photoluminescence in the visible and ultraviolet ranges were experimentally observed. Therefore, the nanosystems are promising in terms of building outbuildings, vibrating "whiter" light [3 – 5].

In [4], a method was developed for producing highly luminescent cadmium sulfide NCs in aqueous-alcoholic polyethylenimine media. In this method, polyethylenimine-stabilized CdS NC columns were added to cadmium sulfide NC columns synthesized in organic polymers. In the studied nanosystems, the optimal and rarefied concentration of cadmium, sulfur and polyethylenimine was maintained, for which the largest luminescent and stable NCs with sizes from 2.0 to 2.3 nm were established. At the same time, the NC dispersion did not exceed (~10 %) in size. The development of the procedure for the synthesis of NCs CdS without intermediary in aqueous solutions of polyethyleneimine, in which mercaptooctate acid was introduced to stabilize NCs in varieties, made it possible to cheaply increase the photoluminescence of NCs CdS [4]. Based on robot guesses, a method for capturing highly luminescent (with quantum yields of the order of 60–70 % at room temperature) CdS NCs with wide emission ranges in the visible and ultraviolet ranges was proposed in [4].

Currently, the absorption of cadmium sulfide by colloidal NCs in aqueous and alcoholic polyethylenimine media has not been sufficiently studied. There are no reviews that describe the optical properties of colloidal NCs of cadmium sulfide in aqueous and alcoholic polyethyleneimine media. The review describes the absorption nature of a nanosystem consisting of colloidal NCs of cadmium sulfide in aqueous and alcoholic polyethyleneimine media.

INTERBAND TRANSITIONS BETWEEN QUANTUM-CONFINED ELECTRON-HOLE STATES IN NANOCRYSTALS

We have experimentally studied a nanosystem consisting of colloidal cadmium sulfide NCs with an average radius $\bar{\boldsymbol{a}}$ in the range

$$\bar{a}_1 \leq \bar{a} \leq \bar{a}_2 \,, \tag{1}$$

where $\bar{\boldsymbol{a}}_{\mathbf{1}} \ = \mathbf{1.0\ nm}$ and $\bar{\boldsymbol{a}}_{\mathbf{2}} = \mathbf{1.15\ nm}$. Colloidal cadmium sulfide NCs were stabilized with polyethyleneimine. A narrow size distribution of NCs was achieved. Let us assume that the colloidal NCs of cadmium sulfide had a shape close to spherical.

It was experimentally established that the edge of the absorption band of colloidal cadmium sulfide NCs was shifted by 0.7 eV towards higher energies compared to the band gap (2.53 eV) of a single crystal of cadmium sulfide [4]. Therefore, the band gap NC of cadmium sulfide was determined by the value $\boldsymbol{E_g}$ =3.23 eV. Let us assume that this shift of the edge of the absorption band was due to the interaction of charge carriers induced at the interface (NC–polyethylimine) with electrons and holes moving in the QD.

Consider a model of a quasi-zero-dimensional nanosystem consisting of a spherical NC with an average radius $\bar{\boldsymbol{a}}$ (in the volume of which there is a cadmium sulfide material with a dielectric constant $\boldsymbol{\varepsilon_2} \ = \mathbf{9}$), An electron and a hole with effective masses move in NC $(\boldsymbol{m_e}/\boldsymbol{m_o})$ = 0.2 and $(\boldsymbol{m_h}/\ \boldsymbol{m_o})$ = 0.7 ($\boldsymbol{m_0}$ is the mass of a free electron), $\boldsymbol{r_e}$ and $\boldsymbol{r_h}$ are the distances of the electron and hole from the center of NC.

Let us study the energy spectrum of electron-hole pairs in NC, in the case when the average radius $\bar{a}$ NC is limited by the condition:

$$a_h < \ \bar{a} < a_e, a_{ex}, \tag{2}$$

where $a_h = (\varepsilon_2\, \hbar^2/m_h\, e^2)$, $a_e = (\varepsilon_2\, \hbar^2/m_e\, e^2)$, $a_{ex} = (\varepsilon_2\, \hbar^2/\ \mu_{ex}\ e^2)$ are the Bohr radii of the hole, electron, and exciton in cadmium sulfide NC, $\mu_{ex} = m_e\, m_h/(m_e + m_h)$ is the reduced exciton mass, e is the electron charge. In the nanosystem we are studying, the values of $a_h = 0.68$ nm, $a_e = 2.39$ nm , $a_{ex} \ = \ 3.06$ nm and $\mu_{ex} = m_e\, m_h/(m_e + m_h) = 0.156\, m_0$. Satisfaction of condition (2) makes it possible to consider the motion of an electron and a hole in NC in the effective mass approximation [7 – 16].

In the given model of the nanosystem in the effective mass approximation, using the triangular coordinate system $r_e = |\,\boldsymbol{r}_e|$, $r_h = |\,\boldsymbol{r}_h|$, $r = |\,\boldsymbol{r}_e - \ \boldsymbol{r}_h|$, we write the Hamiltonian of electron-hole pairs moving in NC in the following form [8, 10 – 16]:

$$H(r_e, r_h) = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e}\cdot\frac{\partial}{\partial r_e} + \frac{r_e^2 - r_h^2 + r^2}{r_e r}\cdot\frac{\partial^2}{\partial r_e \partial r}\right) - \frac{\hbar^2}{2m_h}\left(\frac{\partial^2}{\partial r_h^2} + \frac{2}{r_h}\cdot\frac{\partial}{\partial r_h} + \frac{r_h^2 - r_e^2 + r^2}{r_h r}\cdot\frac{\partial^2}{\partial r_h \partial r}\right) + V_{eh}(r) + U(r_e, r_h, \bar{a}) + E_g, \tag{3}$$

where the first two terms are the operators of the kinetic energy of the electron and hole, the energy of the Coulomb interaction $V_{eh}(r)$ of an electron and a hole is described by the expression

$$V_{eh}(r) = \ -e^2/\varepsilon_2\, r \tag{4}$$

Expressions for the polarization interaction energy $U(r_e, r_h, \bar{a})$ of an electron and a hole with a spherical interface (NC - matrix) (at a relative permittivity $(\varepsilon_2/\varepsilon_1) \gg 1$) were obtained in [9]. Hamiltonian (3) of electron-hole pairs is written under the assumption that the energy bands of electrons and holes are parabolic.

An three-dimensional Wannier – Mott exciton can appear in a nanosystem starting from the radius NC $\bar{a} \geq 2.8\, a_{ex}$ [8, 10 – 15]. When condition (2) is satisfied, an exciton does not arise in the nanosystem. To determine the energy of electron-hole pair in NC, the average radius $\bar{a}$ satisfies condition (2), we will take into account in the Hamiltonian (3) the energy of the Coulomb interaction $V_{eh}(r)$ (4) of an electron and a hole, as well as the energy of the polarization interaction $U(r_e, r_h, \bar{a})$ [9] of an electron and a hole with a spherical interface (NC – matrix). This is due to the fact that in a nanosystem in which the average radius $\bar{a}$ NC is in the interval (2), energies $V_{eh}(r)$ (4) and $U(r_e, r_h, \bar{a})$ [8, 10] are proportional to $(\sim e^2/\varepsilon_2\bar{a})$ and are close in order of magnitude to the energies of size quantization of an electron (hole) in NC.

We determine the energy of the electron – hole pair ground state

$$E_{eh}(\bar{a}, \gamma(\bar{a})) = \langle\, \Psi(r_e, r_h, r)|H(r_e, r_h)|\Psi(r_e, r_h, r))\rangle, \qquad (5)$$

by the variational method. We write the variational wave function of the electron–hole pair ground state (1s-hole state and 1s-electron state) in the nanosystem in the form [14]

$$\Psi(r_e, r_h, r) = A(\bar{a}^2 - r_h^2)(\bar{a}^2 - r_e^2)\left[\left({}^{r_e r_h}/_{\bar{a}}\right)^2 + 2r_e r_h cos\theta + \bar{a}^2\right]^{1/2} \frac{sin(\pi\, r_e/\bar{a})}{r_e} \cdot \frac{sin(\pi\, r_h/\bar{a})}{r_h} exp(-\gamma(\bar{a}) r/\bar{a}) \qquad (6)$$

where A is the normalization coefficient, $\gamma(\bar{a})$ is the variational parameter.

Consider the motion of an electron-hole pair in NC under the assumption that NC is modeled by an infinite spherical potential well. Therefore, the variational function $\Psi(r_e, r_h, r)$ (6) includes the wave functions of a noninteracting electron and hole $(\sim \frac{sin(\pi\, r_e/\bar{a})}{r_e})$, $(\sim \frac{sin(\pi\, r_h/\bar{a})}{r_h})$, moving in an infinite spherical potential well NC. The variational wave function (6) also contains a hydrogen-like wave function $(\sim exp(-\gamma(\bar{a})\, r/\bar{a}))$, which takes into account the Coulomb attraction between an electron and a hole in NC. Furthermore, the polynomials from r_e and r_h enter the variational function (6), which make it possible to eliminate singularities in the functional (9) and obtain the expression for the functional $E_{eh}(\bar{a}, \gamma(\bar{a}))$ (5) of an electron-hole pair in NC in the final analytical form [14].

Upon absorption of a quantum of light with energy

$$\hbar\omega_{eh}(\bar{a}) = E_g + E_{eh}\big(\bar{a}, \gamma(\bar{a})\big), \qquad (7)$$

an electron-hole pair with energy $E_{eh}(\bar{a}, \gamma(\bar{a}))$ (5) is excited in the nanosystem. Let us present the results of a variational calculation of the energy $E_{eh}(\bar{a}, \gamma(\bar{a}))$ (5) of an electron-hole pair ground state in a nanosystem containing cadmium sulfide NC with an average radius $\bar{a}$ (2) (energies (5) are measured from the bottom of the conduction band NC of cadmium sulfide) ((see Table 1) [14]. This nanosystem was experimentally studied in [4].

NUMERICAL RESULTS AND DISCUSSION

It was found that polyethyleneimine-stabilized CdS colloids are characterized by intense photoluminescence, as well as small size of NCs and their narrow size distribution [4]. The edge of the absorption band in the electronic spectra of CdS-polyethylenimine NCs in both aqueous and alcohol solutions was shifted by 0.70 eV towards higher energies compared to bulk cadmium sulfide. The absorption band was characterized by a distinct fine structure. Absorption peaks were obtained with energies $\boldsymbol{E_1}$ = 3.35 eV; $\boldsymbol{E_2}$ = 4.14 eV; $\boldsymbol{E_3}$ = 4.43 eV; $\boldsymbol{E_4}$ = 4.75 eV [4].

Table. The energy $E_{eh}(\bar{a})$ (5) (expressed in eV) of an electron-hole pair ground state and the electron transition energy $\hbar\omega_{eh}(\bar{a})$ (7) (expressed in eV), as a function of the radius $\bar{a}$ (expressed in nm) NC of cadmium sulfide [14].

$\bar{a}$ (nm)	$E_{eh}(\bar{a})$ (eV)	$\hbar\omega_{eh}(\bar{a})$ (eV)
1.0	0.67	3.90
1.15	0.46	3.69

It follows from the Table that when the average radius $\bar{a}$ NC of cadmium sulfide changes in the interval (2), an absorption band with energies lying in the ultraviolet region of the spectrum appears in the conduction band of NC

$$3.69 \text{ eV} \leq \hbar\omega_{eh}(\bar{a}) \leq 3.90 \text{ eV}, \tag{8}$$

of cadmium sulfide [14]. The absorption peak $\boldsymbol{E_1}$ = 3.35 eV falls into the band with energies (8), differing from the theoretical energy value (7) ($\boldsymbol{\hbar\omega_{eh}}$ =3.69 eV) only slightly within ((3.69 eV $-$ $\boldsymbol{E_1})/\boldsymbol{E_1}) \approx \mathbf{0.12}$). The second absorption peak $\boldsymbol{E_2}$ = 4.14 eV also slightly differs from the theoretical energy value (7) ($\boldsymbol{\hbar\omega_{eh}}$ = 3.90 eV) within (($\boldsymbol{E_2} \;\mathbf{- 3.90\ eV})/\boldsymbol{E_2}) \approx \mathbf{0.08}$) [14].

It should be noted that the lowest energy levels $\boldsymbol{E_{eh}(\bar{a},\gamma(\bar{a})}$ (5) of an electron-hole pair ground state in a nanosystem containing cadmium sulfide NC with an average radius $\boldsymbol{\bar{a}}$ (2), were obtained by us by a variational method under the assumption that that the energy bands of electrons and holes are parabolic. The energy values $\boldsymbol{E_{eh}(\bar{a},\gamma(\bar{a}))}$ (5) must satisfy the condition

$$E_{eh}(\bar{a}))/\Delta V \ll 1, \tag{9}$$

where the depth $\boldsymbol{\Delta V}$ of the potential well for electrons moving in cadmium sulfide NC was of the order band gap $\boldsymbol{E_g}$ cadmium sulfide NC [17]. The obtained values of the energies $\boldsymbol{E_{eh}(\bar{a})}$ (5) of an electron-hole pair ground state in the interval $\mathbf{0.46\ eV} \leq \boldsymbol{E_{eh}(\bar{a})} \leq$ 0.67 eV in a nanosystem can be slightly overestimated, since variational calculations of the energies of electron states gave overestimated energies [8, 10 – 15].

The energy levels of the electron-hole pair are $\boldsymbol{E_{eh(1)}}$ = 0.12 eV and $\boldsymbol{E_{eh(2)}}$ = 0.91 eV, which correspond (according to formula (7)) to absorption peaks $\boldsymbol{E_1}$ = 3.35 eV and $\boldsymbol{E_2}$ = 4.14 eV established under the experimental conditions [6], satisfy requirement (9) (the ratios $\boldsymbol{E_{eh(1)}/\Delta V} \cong$ 0.04 and $\boldsymbol{E_{eh(2)}/\Delta V} \cong$ 0.28). Therefore, the energy levels of an electron-hole pair $\boldsymbol{E_{eh(1)}}$ and $\boldsymbol{E_{eh(2)}}$ can be considered the lowest energy levels of an electron-hole pair in a nanosystem. The absorption peaks $\boldsymbol{E_1}$ = 3.35 eV and $\boldsymbol{E_2}$ = 4.14 eV are due to interband electron transitions between the ground ($\boldsymbol{n_h} = \mathbf{1},\ \boldsymbol{l_h} = \mathbf{0}$) quantum – confined hole level located in the NC CdS valence band and the ground ($\boldsymbol{n_e} = \mathbf{1},\ \boldsymbol{l_e} = \mathbf{0}$) quantum – confined electron level located in the NC conduction band of cadmium sulfide ($\boldsymbol{n_{e(h)}}$ и $\boldsymbol{l_{e(h)}}$ are the principal and orbital quantum numbers of the electron (holes)) [14].

As for the experimental absorption peaks $\boldsymbol{E_3}$ =4.43 eV and $\boldsymbol{E_4}$ =4.75 eV [6], they correspond to the energy levels of the electron-hole pair $\boldsymbol{E_{eh(3)}} = \mathbf{1.2\ eV}$ and $\boldsymbol{E_{eh(4)}} = \mathbf{1.52\ eV}$ (according to formula (7)) in a nanosystem. Such energy levels are not low-excited levels in the nanosystem (condition (9) is not satisfied). Therefore, within the framework of our variational calculations, we failed to interpret these absorption peaks [14].

The experimental absorption peaks $\boldsymbol{E_3} = 4.43$ eV and $\boldsymbol{E_4} = 4.75$ eV [6], can apparently be caused by interband electron transitions between highly excited quantum-confined hole levels located in the valence band of the CdS NC and highly excited quantum-confined electron levels located in the conduction band of a cadmium sulfide NC [14].

In experimental work [1 – 3, 5], absorption bands in the visible region of the spectrum were observed in nanosystems containing CdS quantum dots. In contrast to [1 – 3, 5], in [4] it was established that the edge of the absorption band in the nanosystem shifted by 0.7 eV towards higher energies (compared to the band gap of a cadmium sulfide single crystal). This shift led to the appearance of broad absorption bands in the ultraviolet region of the spectrum. Such an absorption band with energies (7) lying in the ultraviolet region of the spectrum has been theoretically determined by us [14].

CONCLUSIONS

A mechanism is proposed that describes the absorption of the considered nanosystem in the ultraviolet spectral ranges. It is shown that the absorption peaks of the nanosystem are caused by interband electron transitions from the energy quantum-confined level lying in the valence band of the CdS NC to the energy quantum-confined level located in the conduction band of the cadmium sulfide NC. It has been established that the formation of the energy quantum-confined levels of an electron and a hole in a CdS nanocrystal, is significantly affected by the energy of the Coulomb electron-hole interaction, as well as the energy of the polarization interactions of the electron and hole with the interface (nanocrystal – matrix).

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УДК 621.315.5.001:53 *DOI: 10.15407/Surface.2024.16.037*

ОПТИЧНА СПЕКТРОСКОПІЯ НАНОКРИСТАЛІВ СУЛЬФІДУ КАДМІЮ В УЛЬТРАФІОЛЕТОВОМУ СПЕКТРІ

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У міні-огляді розглядаються теоретичні дослідження деяких оптичних властивостей нанокристалів сульфіду кадмію в ультрафіолетовому спектрі. Описано варіаційний метод, за допомогою якого отримано енергію основного стану електронно-діркової пари, як функцію радіуса нанокристала сульфіду кадмію в наближенні ефективної маси. Запропоновано механізм, що описує поглинання розглянутої наносистеми в ультрафіолетовому діапазоні спектра. Показано, що піки поглинання наносистеми зумовлені міжзонними переходами електронів з квантово-вимірного рівня енергії, що лежить у валентній зоні НК CdS, на енергетичний квантово-вимірний рівень, розташований у зоні провідності НК сульфіду кадмію. Встановлено, що на формування квантово-вимірних рівнів енергії електрона та дірки в нанокристалі CdS суттєво впливає енергія кулонівської електронно-діркової взаємодії, а також енергія поляризаційних взаємодій електрон і дірка з поверхнею поділу (нанокристал – матриця).

Ключові слова: *електронні переходи, квантово-вимірні стани електронів, кулонівська електронно-діркова взаємодія.*