

S.I. Pokytnii<sup>1</sup>, A.D. Terets<sup>1,2</sup>

## OPTICAL ABSORPTION BY TITANIUM DIOXIDE NANOCRYSTALS

<sup>1</sup> *Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine  
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: pokutnyi.serg@gmail.com*

<sup>2</sup> *Faculty of Physics, Taras Shevchenko National University of Kyiv  
4 Academician Glushkov Avenue, Kyiv, 03127, Ukraine*

Using a variational method within the framework of the effective mass approximation, using a triangular coordinate system of an electron, hole, and exciton moving in a titanium dioxide quantum dot, the exciton energy spectrum was obtained as a function of the radius  $a$  of the quantum dot. The variational wave function of the exciton contained factors that took into account the motion of an electron and a hole in a potential well of infinite depth of a quantum dot, as well as the form of a hydrogen-like wave function. It is shown that the occurrence of an exciton in a quantum dot has a threshold character. An exciton, as a bound state of an electron and a hole, is formed starting from a certain critical radius  $a_c$ , the value of which exceeds the Bohr radius of the exciton in titanium dioxide. The exciton energy levels are located in the band gap of the titanium dioxide quantum dot. In this case, with an increase in the radius  $a$  of the quantum dot (so that  $a \geq a_c$ ), a band of exciton states appears in the band gap of the titanium dioxide quantum dot.

The mechanism for the formation of optical absorption spectra in nanosystems containing titanium dioxide nanocrystals are presented. It is found that the optical absorption of anatase NC, which was observed under the experimental conditions, was due to the appearance of an exciton in the NC. Using the variational calculation of the energy spectrum of an exciton in NC, the position of the absorption peak of NC anatase was determined. This absorption peak differs slightly from the absorption peak, which was obtained in the experimental work.

**Keywords:** titanium dioxide nanocrystals, exciton state, absorption peak, mechanism of optical absorption

### INTRODUCTION

Researches of quasi-zero-dimensional nanosystems consisting of semiconductor titanium dioxide nanocrystals (NCs) are receiving increased attention due to their unique photoluminescent properties, the ability to emit light efficiently in the visible or near-infrared ranges at room temperature [1–4].

In experimental work [1], the optical properties of semiconductor nanosystems based on titanium dioxide NCs with an average radius not greater than  $a = 22$  nm were explored. It has been found that such nanosystems titanium dioxide NCs have a broad absorption band in the visible and near-infrared wavelength regions.

In [1], the absorption of light in the energy range (2.6–3.7 eV) by NCs of anatase (titanium dioxide) with an average radius of  $a_1 = 11$  nm was studied. The  $E_0 = 3.10$  eV absorption peak was observed in the nanosystem. We will assume that NCs have a spherical shape.

At the same time, the nature of the optical absorption of on titanium dioxide NCs was not investigated in [1]. Therefore, in this paper, the

mechanism for the formation of optical absorption spectra in nanosystems containing titanium dioxide NCs are presented.

### THE ENERGY OF THE GROUND STATE OF AN EXCITON IN A NANOCRYSTAL

We consider a model nanosystem [5] that consists of a spherical NC (in the volume which contains a semiconductor material with a permittivity  $\varepsilon$  and radius  $a$ ). In the volume this NC are electron and hole with effective mass  $m_e$  and  $m_h$  ( $r_e$  and  $r_h$  are the distance between electron/hole and center of NC). We also assume that the energy bands of electrons and holes are parabolic.

To excite the ground state of the exciton ( $n = 1$ ) (where  $n$  is the principal quantum number of the exciton), the nanosystem must absorb a light quantum with energy

$$\hbar\omega_{ex}(a) = E_g - |E_{ex(1)}(a)| \quad (1)$$

where  $E_g$  is the bandgap width of the NC,  $E_{ex(1)}(a)$  is the exciton binding energy.

In the studied model of the nanosystem in the the effective mass approximation, when the triangular coordinate system  $r_e = |r_e|$ ,  $r_h =$

$|r_h|$ ,  $r = |r_e - r_h|$  is employed starting at the NC center, the Hamiltonian of the exciton in the NC is [5]:

$$H(\mathbf{r}_e, \mathbf{r}_h) = -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e} \cdot \frac{\partial}{\partial r_e} + \frac{r_e^2 - r_h^2 + r^2}{r_e r} \cdot \frac{\partial^2}{\partial r_e \partial r} \right) - \frac{\hbar^2}{2m_h} \left( \frac{\partial^2}{\partial r_h^2} + \frac{2}{r_h} \cdot \frac{\partial}{\partial r_h} + \frac{r_h^2 - r_e^2 + r^2}{r_h r} \cdot \frac{\partial^2}{\partial r_h \partial r} \right) - \frac{\hbar^2}{2\mu_{ex}} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial}{\partial r} \right) + V_{eh}(r) + E_g, \quad (2)$$

where the first three terms are the operators of kinetic energy of the electron, hole, and exciton,  $\mu_{ex} = m_e m_h / (m_e + m_h)$  is the reduced exciton mass. In the Hamiltonian (2) the electron – hole Coulomb interaction energy  $V_{eh}(r)$  is described by the formula

$$V_{eh}(r) = -(e^2/\varepsilon)(r_e^2 - 2r_e r_h \cos\theta + r_h^2)^{-1/2}, \quad (3)$$

where  $\theta$  is the angle between the radius – vectors  $\mathbf{r}_e$  electron and  $\mathbf{r}_h$  hole.

We estimate the energy  $E_1(a)$  of the exciton ground state

$$E_{ex(1)}(a, \mu(a)) = \langle \Psi_{ex}(a, \mu(a)) | H(r_e, r_h) | \Psi_{ex}(a, \mu(a)) \rangle \quad (4)$$

by the variational method. We write the variational radial wave function of the exciton ground state (the 1s state of the hole and the 1s state of the electron) in the NC of radius  $a$  as:

$$\Psi_{ex}(r_e, r_h, r) = A (a - r) \exp\left(-\frac{\mu(a)}{\mu_{ex}} \cdot \frac{r}{a_{ex}}\right) \frac{\sin(\pi r_e/a)}{r_e} \cdot \frac{\sin(\pi r_h/a)}{r_h}, \quad (5)$$

where  $A$  is the normalization coefficient,  $\mu(a)$  is the variational parameter,  $a_{ex} = \varepsilon \hbar^2 / \mu_{ex} e^2$  is the Bohr radius of a exciton in a NC. Here the coefficient  $A$  is determined from the condition of normalization of the exciton wave function (5):

$$\int_0^a r_e dr_e \int_0^a r_h dr_h \int_0^{r_e+r_h} dr r (\Psi_{ex}(r_e, r_h, r))^2 = 1. \quad (6)$$

At  $a \ll a_{ex}$ , the size-quantization energy of the electron (hole) in a NC ( $\sim \hbar^2 / 2m_{e(h)} a^2$ ) is high compared to the energy of the electron – hole Coulomb interaction (3). Therefore, in the first-order approximation, the Coulomb interaction (3) can be disregarded. In this case, the major

contribution to the exciton Hamiltonian (2) for the NC of small radius  $a \ll a_{ex}$  is made by the kinetic energy of the noninteracting electron and hole. In this context, the variational function of the exciton (5) involves the wave functions of the noninteracting electron and hole ( $\sim \frac{\sin(\pi r_e/a)}{r_e}$ ), ( $\sim \frac{\sin(\pi r_h/a)}{r_h}$ ) in motion within the infinitely deep spherical potential well simulating the NC. With increasing NC radius  $a$ , such that  $a$  becomes larger than  $a_{ex}$ , the exciton appears in the NC [3]. Because of this, the variational wave function of the exciton (5) involves the eigenfunction of the Wannier – Mott exciton ( $\sim \exp\left(-\frac{\mu(a)}{\mu_{ex}} \cdot \frac{r}{a_{ex}}\right)$ ). Since the electron and hole cannot penetrate into the NC, then at the interface (NC is the matrix) at  $r = a$ , the exciton wave function (5)  $\Psi_{ex}(r_e, r_h, r) = 0$ .

## NUMERICAL RESULTS AND DISCUSSION

Let us present the results of the variational calculation of the energy  $E_{ex(1)}(a)$  (4) of the ground state of the exciton are obtained (see Table) for a nanosystem containing anatase NC (with permittivity  $\varepsilon = 3.5$ ; effective mass of the electron is  $(m_e/m_o) = 10$  and effective mass of the hole is  $(m_h/m_o) = 0.8$  ( $m_o$  is mass of a free electron). This nanosystem was studied experimentally in [1]. The anatase NC radii  $a$  were in this case in the range determined by the inequality

$$0.85 \text{ nm} \leq a \leq 24 \text{ nm}. \quad (7)$$

It follows from Table that the exciton, which is the bound state of the electron-hole pair, in the nanosystem are formed near the anatase NC spherical surface at distances beginning from the NC radius  $a \geq a_c = 3.4 a_{ex} = 0.85 \text{ nm}$ . Such exciton states at  $a \geq a_c$  are in the range of

negative energies (measured from the bottom of the anatase NC conduction band  $E_g = 3.44$  eV). The appearance of an exciton in the NC is due to the fact, that at  $a \geq a_c$  the electron – hole Coulomb interaction energy  $|V_{eh}(a)|$  (3) was greater than the kinetic energy of the exciton ( $\sim \frac{\hbar^2}{2\mu_{ex}a^2}$ ). The energy levels of the exciton at  $a \geq a_c$  are located in the band gap of the anatase NC. Beginning with the anatase NC radii  $a \geq a_{c(1)} = 24$  nm, exciton ground state energy  $E_{ex(1)}(a)$ , asymptotically tends to the value ( $E_{ex} = -0.823$  eV), which characterizes the binding energy of a 3D exciton (see Table). As such, with an increase in the radius  $a$  of the NC, so that  $a \geq a_c$ , an exciton band with a width of no greater than  $E_{ex} = 0.823$  eV, appears in the nanosystem, located in the bandgap of the NC (under the bottom of the conduction band NC) (see Table).

**Table.** The energy  $E_{ex(1)}(a)$  (4) (expressed by eV) of the ground state of an exciton, and the energy of exciton transition  $\hbar\omega_{ex}(a)$  (1) (expressed by eV), as a function of the anatase NC radius  $a$  (expressed by nm),  $a_{ex} = 0.25$  nm is the Bohr radius of a exciton in a NC

$a$ , nm	$E_{ex(1)}(a)$ , eV	$\hbar\omega_{ex}(a)$ , eV
0.85	0	3.44
3	-0.14	3.30
5	-0.28	3.16
7	-0.41	3.03
9	-0.528	2.912
11	-0.65	2.79
15	-0.75	2.69
20	-0.80	2.64
24	-0.823	2.617

In the experimental work [1], a broad absorption band was observed in the visible region of the spectrum in the range

$$2.60 \text{ eV} \leq \Delta E \leq 3.70 \text{ eV} \quad (8)$$

in the nanosystem under study. It follows from the results of variational calculations of the exciton ground state energy  $E_{ex(1)}(a)$  (4) in the nanosystem, that as the anatase NC radii  $a$  change over the interval (7), an absorption band appears in the visible region of the spectrum with a width (see Table):

$$2.62 \text{ eV} \leq \hbar\omega_{ex}(a) \leq 3.44 \text{ eV} \quad (9)$$

where the exciton transition energy  $\hbar\omega_{ex}(a)$  (1).

In the visible region of the spectrum in the energy interval (15), the absorption mechanism in a nanosystem containing the anatase NC with radii  $a$  in the interval (7) is caused by the transition of an electron from the ground quantum level in the valence band of the NC to the ground level of the exciton  $E_{ex(1)}(a)$  (4) located in the bandgap of the NC. The absorption peak  $\hbar\omega_{ex}(a_1)$  (1) in a nanosystem containing anatase NCs with an average radius  $a_1 = 11$  nm, as follows from the Table, takes a value  $\hbar\omega_{ex}(a_1) = 2.79$  eV. This absorption peak  $\hbar\omega_{ex}(a_1) = 2.79$  eV differs slightly (within 11 %) from the absorption peak  $E_0 = 3.10$  eV, which was obtained in the experimental work [1]. Thus, the absorption band (9) is almost completely included in the absorption band (8), which was observed in the experimental work [1].

## CONCLUSION

It is found that the optical absorption of anatase NC, observed under the experimental conditions [1], was due to the appearance of an exciton in the NC. Using the variational calculation of the energy spectrum of an exciton in NC, the position of the absorption peak of NC anatase was determined. This absorption peak differs slightly from the absorption peak, which was obtained in the experimental work [1].

## Оптичне поглинання нанокристаллами діоксиду титану

С.І. Покутній, А.Д. Терець

Інститут хімії поверхня ім. О.О. Чуйка Національної академії наук України  
вул. Генерала Наумова, 17, Київ, 03164, Україна, pokutnyi.serg@gmail.com  
Фізичний факультет, Київський національний університет імені Тараса Шевченка  
просп. Академіка Глушкова, 4, Київ, 03127, Україна

Варіаційним методом у рамках наближення ефективної маси, з використанням триангулярної системи координат електрона, дірки та екситону, що рухаються в квантовій точці діоксиду титану, отримано енергетичний спектр екситону, як функції радіуса  $a$  квантової точки. Варіаційна хвильова функція екситону містила множники, які враховували рух електрона та дірки у потенційній ямі нескінченної глибини квантової точки, а також вид воднеподібної хвильової функції. Показано, що виникнення екситону у квантовій точці має пороговий характер. Екситон, як зв'язаний стан електрона і дірки, утворюється, починаючи з деякого критичного радіуса  $a$ , який перевищує борівський радіус екситону в діоксиді титану. Енергетичні рівні екситону розташовані в забороненій зоні квантової точки діоксиду титану. При цьому зі збільшенням радіуса  $a$  квантової точки (так що  $a \geq a_c$ ) з'являється зона екситонних станів в забороненій зоні квантової точки діоксиду титану.

Представлено механізм формування спектрів оптичного поглинання в наносистемах, що містять нанокристали діоксиду титану. Встановлено, що оптичне поглинання нанокристалла анатазу, яке спостерігалось в умовах експерименту, зумовлено появою екситону в нанокристалі. За допомогою варіаційного розрахунку енергетичного спектра екситона в нанокристалі визначено положення піку поглинання нанокристалла анатазу. Цей пік поглинання слабо відрізняється від піку поглинання, отриманого в експериментальній роботі.

**Ключові слова:** нанокристали діоксиду титану, екситонний стан, пік поглинання, механізм оптичного поглинання

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