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Research Article

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Optical Absorption in Titanium Dioxide Nanocrystals

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Abstract

A mechanism for the formation of an optical absorption edge in nanosystems containing titanium dioxide nanocrystals are prsented. It has been established that the optical absorption of nanosystems, observed under experimental conditions, is caused to the exciton transitions in titanium dioxide nanocrystals.

Keywords: Exciton Ground State, Variational Method, Coulomb Interaction Optical Absorption, Titanium Dioxide Nanocrystals.

1. Introduction

Titanium dioxide nanocrystals (NCs) are intensively studied, since they absorb and emit in the optical region [1-6]. In experimental works [3-5], the optical properties of nanosystems based on spherical titanium dioxide NCs were explored. The average radius of these NCs is $a \leq 22$ nm. In [3-5], the absorption of light in the energy range (from 2.6 eV to 3.7 eV) by NCs of anatase (titanium dioxide) with an average radius of was studied. The absorption peak was observed in the nanosystem.

At the same time, the nature of the optical absorption of on titanium dioxide NCs was not investigated in [3-5]. Therefore, in this work, we describe the nature of the optical absorption of titanium dioxide NCs. It is shown that the positions of the absorption peaks in NCs, which we obtained theoretically, differs slightly from the experimental absorption peaks.

2. Exciton ground state energy in nanocrystal

In a nanosystem containing spherical NCs with an average radius a, when a light quantum with the energy is absorbed

$$\hbar\omega_{ex}(a) = E_g - \left|E_{ex(1)}(a)\right|, \qquad (1)$$

the exciton ground state ($n = 1$) (where n is the principal quantum number of the exciton) is excited. In (1) E_g is the bandgap width of the NC, $E_{ex}(1)$ (a) is the exciton binding energy.

In the effective mass approximation, assuming that the energy bands of electrons and holes are parabolic, we write the Hamiltonian of the exciton in the NC [7, 8]:

$$H(\boldsymbol{r_e}, \boldsymbol{r_h}) = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e}\cdot\frac{\partial}{\partial r_e} + \frac{r_e^2 - r_h^2 + r^2}{r_e r}\cdot\frac{\partial^2}{\partial r_e \partial r}\right) - \frac{\hbar^2}{2m_h}\left(\frac{\partial^2}{\partial r_h^2} + \frac{2}{r_h}\cdot\frac{\partial}{\partial r_h} + \frac{r_h^2 - r_e^2 + r^2}{r_h r}\cdot\frac{\partial^2}{\partial r_h \partial r}\right) -$$

$$\frac{\hbar^2}{2\mu_{ex}}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial}{\partial r}\right) + V_{eh}(r) + E_g, \qquad (2)$$

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 NC (m_e and m_h is the effective masses of the electron and hole, r_e and r_h are the distance between electron/hole and center of NC, $r = \left|r_e - r_h\right|$), the energy of the Coulomb interaction between an electron and a hole

$$V_{eh}(r) = -e^2/\varepsilon r \qquad (3)$$

In (3) ε is the permittivity NC. We estimate the energy E1 (a) of the exciton ground state

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

by the variational method, where is the variational wave function $\Psi_{ex}(r_e, r_h, r)$ written 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.

3. Numerical Results and Discussion

Let us present the results of the variational calculation of the energy $E_{ex}(1)$ (a) (4) of the exciton ground state are obtained (see Table 1) for a nanosystem containing anatase NC (with permittivity $\varepsilon = 3.5$; $(m_e / m_o) = 10$ and $(m_h / m_o) = 0.8$ (m_o is mass of a free electron). This nanosystem was studied experimentally in [3-5]. The anatase NC radii a were in this case in the range determined by the inequality

$$0.85 \text{ nm} \le a \le 24 \text{ nm} \quad (6)$$

An exciton appears in an anatase NC with an average radius $a \ge 3.4\, a_c = 3.4\, a_{ex} = 0.85$ nm (see Table 1). In this case, in the anatase NC with an average radius $a \ge a_c$ the electron - hole Coulomb interaction energy $\left| V_{eh}(a) \right|$ (3) prevailed over the kinetic exciton energy. The exciton is localized in the NC bandgap and has a negative energy relative to the NC bottom of the anatase conduction band $E_g = 3.44$ eV (see Table 1). Beginning with the anatase NC radii $a \ge a_{c(1)}$ 24 nm, exciton ground state energy $E_{ex(1)}$ (a), asymptotically tends to the exciton binding energy ($E_{ex} = -0.823$ eV) (see Table 1).

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

Table 1: The energy $E_{ex(1)}$ (a) (4) (expressed by eV) of the exciton ground state, 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.

The absorption band in the range

$$2.60 \text{ eV} \le \Delta E \le 3.70 \text{ eV} \quad (7)$$

was established in experimental works [3-5]. In the visible region of the spectrum, when the NC radii a change in the range (6), an absorption band with a width (see Table 1)

$$2.62 \text{ eV} \le \hbar\omega_{ex}(a) \le 3.44 \text{ eV}, \quad (8)$$

where the exciton transition energy $\hbar_{\omega ex}(a_1)$ (1). This absorption band in the NC was obtained using a variational calculation of the exciton energy (4).

The absorption peak $\hbar_{\omega ex}(a_1)$ (1) in anatase NC with an average radius $a_1 = 11$ nm takes a value $\hbar_{\omega ex}(a_1) = 2.79$ eV (see Table 1). This absorption peak $\hbar_{\omega ex}(a_1)$ differs slightly (within 11%) from the absorption peak $E_o = 3.10$ eV, which was obtained in the experimental works [3-5]. The absorption band (8) is almost completely included in the absorption band (7), which was observed in the experimental works [3-5].

4. Conclusion

It has been established that the formation of an optical absorption edge in a nanosystem, observed under experimental conditions

[3-5], is caused by the transition of an electron from the ground quantum level from the valence band of the NC to the exciton ground level located in the bandgap of the NC. Using the variational calculation of the energy of the exciton ground state 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 works [3-5]. The results obtained, apparently, will solve the problem of developing the fundamental and applied foundations of a new generation of efficient photodetectors based on nanostructures with titanium dioxide NCs.

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