

Exciton states of titanium dioxide nanocrystals

SERHI I. POKUTNII^{1,2}, ANDRZEJ RADOSZ^{1,*}

¹Department of Quantum Technologies, Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
e-mail: Andrzej.Radosz@pwr.edu.pl

²Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 17 General Naumov Str., Kyiv 03164, Ukraine
e-mail: pokutnyi.serg@gmail.com

*Corresponding author: Andrzej.Radosz@pwr.edu.pl

Using a variational method within the framework of an effective mass approximation, applying a triangular coordinate system of an electron, a hole and an exciton moving in a titanium dioxide nanocrystal, an exciton energy spectrum was obtained as a function of a radius of the nanocrystal particle. It was established that the optical absorption of anatase nanocrystal, observed in the experiment, was due to the appearance of an exciton in the nanocrystal. Using a variational calculation of the energy spectrum of the exciton in the nanocrystal, a position of an absorption peak was determined.

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

1. Introduction

Studies of quasi-zero-dimensional nanosystems consisting of semiconductor titanium dioxide nanocrystals (NCs) have been receiving increased attention due to their unique photoluminescent properties, the ability to efficiently emit light in the visible or near-infrared ranges at room temperature [1-9].

In experimental works [3-5], the optical properties of semiconductor nanosystems based on titanium dioxide NCs with an average radius of quantum dot not greater than $a = 22$ nm were explored. It was found that such nanosystems have a broad absorption band in the visible and near-infrared wavelength regions.

In [3-5] the absorption of light in the energy range from 2.6 to 3.7 eV, by NCs of anatase (titanium dioxide) with an average quantum dot radius of $a_1 = 11$ nm was studied. The $E_0 = 3.10$ eV absorption peak was observed. We will assume that NCs are small particles of a spherical shape.

Yet the nature of the optical absorption of on titanium dioxide NCs was not investigated in [3-5]. Therefore, in this paper, the mechanism for the formation of optical absorption spectra in nanosystems containing titanium dioxide NCs is presented.

2. The present status of titanium dioxide nanomaterials research

Nanocrystalline titanium dioxide (TiO_2) has many applications due to its optical, thermal, photocatalytic, and electrophysical properties [1-20]. For instance, nanocrystalline TiO_2 is utilized in dye-sensitized solar cells, hydrogen production and storage processes, sensors, rechargeable batteries, self-cleaning and antibacterial surfaces. Currently, the most active research is related to the photocatalytic activity of TiO_2 nanoparticles for the environmental cleanup of organic pollutants. Due to the chemical stability, non-toxicity, and low cost TiO_2 is considered the most promising photocatalytic for the degradation of pollutants in water and in air [1-4, 9-12, 15].

Titanium dioxide has three naturally occurring polymorphs: rutile, anatase with the tetragonal crystal lattice, and brookite with the orthorhombic crystal lattice [16-18]. Rutile is thermodynamically more stable than anatase and brookite, which can be irreversibly transformed into the stable rutile phase by heat treatment in the temperature range from 400 to 1200 °C. Herewith, the temperature value is determined not only by the material synthesis technique but also by the method of determination of the transition temperature [19, 20]. The stability of crystalline modifications also depends on the size of crystallites. According to the data reported in [19], anatase has higher thermodynamic stability if the particle size of TiO_2 does not exceed 35 nm.

The use of organic extracts based on saturated fatty acids as a new type of precursors is proposed in the framework of the extraction-pyrolytic method (EPM) to produce oxide materials for various functional purposes [17-20]. Synthesis of complex oxide materials by EPM includes the following main steps extraction of metal ions from an aqueous solution with carboxylic acid (with or without a diluent), mixing the extracts in the required ratio and subsequent pyrolysis. Herewith, EPM ensures the homogeneity of the materials produced, does not require the use of complex equipment and high costs for the raw materials. The advantages of the method also include its versatility in production of nanocrystalline materials both as powders and films on various substrates and composites [17-20].

In [11], TiO_2 with various Eu additions was obtained by the EPM using mixtures of Ti- and Eu-containing extracts based on valeric acid. In addition, the influence of the ratio of metals in the initial mixture of precursors and the temperature of its pyrolysis on the phase composition, photocatalytic and luminescent properties of the final nanocrystalline powders.

The enhanced mechanical and thermal properties of TiO_2 nanocomposites reinforced with photo-resin via 3D printing were recently presented in [21]. Another interesting report [22] is about an excellent UV shielding properties of poly(methylmethacrylate) PMMA/oxide nanocomposites with different types of nanoparticles, which could be used in variety of applications such as sunscreens, aerospace, and several other fields related to UV photodegradation. It is important to note that the thermal and mechanical properties of PMMA-titania nanocomposites and their degradation behavior was discussed in detail in [21]. Note also that nanoporous anatase layers may become interesting for nonlinear optical applications [22].

In paper [12] there were presented the results of studies of the efficiency of using ionizing radiation to modify the surface morphology and structural properties of TiO_2 thin films, and the effect of ion modification on the photocatalytic activity of Rhodamine decomposition was discussed. Structural and morphological changes in thin films were characterized by irradiation with doses of 10^{14} – 10^{16} ion/cm² using scanning electron microscopy, atomic force microscopy, energy-dispersive analysis and X-ray diffraction. Modification of thin films by ion irradiation leads to a change in grains orientation, a decrease in their size, and an increase in the active surface area. Formation of grains of preferred orientation at high radiation doses is caused both by grains rotation as a result of distorting and deformation factors caused by radiation, and by grains partial fragmentation. It was shown that in the case of modified samples of thin films, not only an increase in the rate decomposition reaction constant by 2–4.5 times compared with the initial samples, but also the degree of mineralization is observed. According to the data obtained, the maximum value of mineralization as a result of photocatalytic reactions for initial films was no more than 75–76%. While for irradiated samples, this value varies from 83 to 90% depending on the irradiation dose. For modified films, an increase in crack resistance and resistance to degradation to prolonged tests of photocatalytic activity is observed.

In [15], the models of chlorine adatoms placed on the rutile $\text{TiO}_2(110)$ /water interface were constructed using *ab initio* methods. The time-dependent spatial charges, bond-lengths of water molecules, and Hirshfeld charges were calculated by real-time-time-dependent density functional theory and the Ehrenfest dynamics theory for investigating the excited state nonadiabatic dynamics of water dissociation. This study presents two photoinduced water-splitting pathways related to chlorine and analyzes the photogenerated hole along the reactions. The first step of water dissociation relies on the localized competition of oxygen charges between the dissociated water and the bridge site of TiO_2 for transforming the water into hydroxyl and hydrogen by photoinduced driving force.

In [15], the effect of impact of Cl adatoms on the water dissociation under photoexcitation was discussed. The procedures consisted of the following steps: the initial surface models were subjected to an *ab initio* molecular dynamics to allow the catalytic systems to reach the desired temperature; the bond lengths of hydroxyl were analyzed to assess the impact of single Cl adatoms on water dissociation. The excitation energy was limited to the energy near the edge of the visible-light to UV regions, corresponding to the band gap of TiO_2 .

3. The energy of the ground state of an exciton in a nanocrystal

We will consider a model nanosystem [23] that consists of a spherical particles (quantum dots), of a semiconductor material with a permittivity ϵ and radius a . In a volume of such a NC there is an electron and a hole with effective mass m_e and m_h , respectively (r_e/r_h denotes the distance between electron/hole and a center of NC particle). We will also assume that the energy bands of electrons and holes are of parabolic shape.

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

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

where E_g is the bandgap width of a NC, $E_{\text{ex}(1)}(a)$ 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 originating at the NC center, the Hamiltonian of the exciton in the NC is [24-26]:

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

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

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

where θ is an angle between the electron and the hole radius-vectors \mathbf{r}_e and \mathbf{r}_h , respectively.

We estimate the energy of the exciton ground state

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

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

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

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

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

At $a \ll a_{\text{ex}}$, the size-quantization energy of the electron (hole) in a NC $\left(\sim \frac{\hbar^2}{2m_{e(h)}a^2} \right)$

is large compared to the energy of the electron-hole Coulomb interaction (3). Therefore, in the first-order approximation, the Coulomb interaction term (3) can be neglected. In this case, the major contribution to the exciton Hamiltonian (2) for the NC of small radius comes from the kinetic energy of the noninteracting electron and hole. In this context, the variational wave function of the exciton (5) involves the wave functions of electron and hole $\left(\sim \frac{\sin(\pi r_e/a)}{r_e} \right)$, $\left(\sim \frac{\sin(\pi r_h/a)}{r_h} \right)$ confined within an infinitely deep spherical potential well simulating the NC. With increasing NC's radius a , such that a becomes larger than a_{ex} , the exciton appears in the NC [11]. Because of this, the variational wave function of the exciton (5) involves the eigenfunction of the Wannier-Mott exciton $\left(\sim \exp\left(-\frac{\mu(a)}{\mu_{\text{ex}}} \frac{r}{a_{\text{ex}}}\right) \right)$. Since the electron and the hole cannot penetrate the NC, the interface (NC is the matrix) at $r = a$ is imposed, $\Psi_{\text{ex}}(r_e, r_h, r) = 0$.

4. Numerical results and discussion

Let us present the results of the variational calculation of $E_{\text{ex}(1)}(a)$, the energy of the ground state of the exciton (see Table 1) for a nanosystem containing anatase NC (with permittivity $\varepsilon = 3.5$); effective mass of the electron is $(m_e/m_0) = 10$ and effective mass of the hole is $(m_h/m_0) = 0.8$ (m_0 denotes mass of a free electron). (Such a nanosystem was studied experimentally in [3-5].) The anatase NC radii a were confined in this case to the following range

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

T a b l e 1. The energy $E_{\text{ex}(1)}(a)$ (4) of the ground state of an exciton, and the energy of exciton transition $\hbar\omega_{\text{ex}}(a)$ (1), as a function of the anatase NC radius a , $a_{\text{ex}} = 0.25$ nm is the Bohr radius of an exciton in a NC's particle.

| a [nm] | $E_{\text{ex}(1)}(a)$ [eV] | $\hbar\omega_{\text{ex}}(a)$ [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 |

It follows from the results presented in Table 1 that the exciton, which is the bound state of the electron-hole pair is formed near the anatase NC (spherical) surface at distances ranging from the NC radius $a \geq a_c = 3.4 a_{ex} = 0.85$ nm. Such exciton states belong to 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 results from the fact, that for $a \geq a_c$ the electron-hole Coulomb interaction energy $|V_{eh}(a)|$ (3) is greater than the kinetic energy of the exciton $\left(\sim \frac{\hbar^2}{2\mu_{ex}a^2} \right)$. The energy levels of the exciton (for $a \geq a_c$) 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 1). As such, with a decrease of the radius a of the NC, so that $a \geq a_c$, an exciton band of a width no greater than $E_{ex} = 0.823$ eV, appears to be located in the bandgap of the NC (under the bottom of the conduction band NC) (see Table 1).

In the experimental research [3-5], 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 the study. It follows from the results of variational calculations of the exciton ground state energy $E_{ex(1)}(a)$, that as the anatase NC radii a varies within the interval (7), an absorption band appears in the visible region of the spectrum with a width (see Table 1):

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

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

In the visible range of the spectrum, 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 state level in the valence band of the NC to the ground state of an 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, takes, as follows from Table 1, the value $\hbar \omega_{ex}(a_1) = 2.79$ eV. This value only slightly differs, within 11%, from the absorption peak value $E_o = 3.10$ eV, which was experimentally observed [3-5]. Thus, the absorption band (9) is completely confined within the experimentally observed absorption band (8).

5. Conclusion

Using a variational method within the framework of an effective mass approximation and applying a triangular coordinate system of an electron, a hole, and an exciton moving in a titanium dioxide NC, the exciton energy spectrum was obtained as a function of the radius a of the NC. 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 an infinite depth of a NC, as well as the form of a hydrogen-like wave function. It is shown that the occurrence of an exciton in a NC 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 that way it has been shown for the first time that with an increase of the radius a of the NC (so that $a \geq a_c$), a band of exciton states appears in the bandgap of the NC titanium dioxide.

The mechanism of formation of optical absorption spectra in nanosystems containing titanium dioxide NCs is proposed. It is established that the optical absorption of anatase NC, which was experimentally observed [3-5], is a result of the appearance of an exciton in the NC. Position of the absorption peak of NC anatase was determined by using variational calculation – this outcome differs slightly from the position of absorption peak, which was obtained in the experimental works [3-5].

The results obtained in this paper will make it possible to develop a fundamental approach allowing to create a new generation of effective light-emitting and photodetector devices based on titanium dioxide heterostructures.

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