

## **Photoelectrochemical properties of films based on TiO<sub>2</sub> nanotubes modified with BiVO<sub>4</sub> and V<sub>2</sub>O<sub>5</sub>**

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By methods of anodizing and ion layering were obtained films TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>/BiVO<sub>4</sub>. With help of spectral studies of photoelectrochemical and optical properties, the band gap and quantum yield of photoelectrochemical current were determined depends on the ratio of films thickness and the parameters of their synthesis. It is shown, that at synthesized structures UV component quantum yield photoelectrode decreases and contribution of visible light increases.

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### **Introduction**

One of the promising and simple to obtain materials for converting solar energy into electricity are TiO<sub>2</sub> and BiVO<sub>4</sub> [1,2]. In order to increase the efficiency of energy conversion of sunlight on these semiconductors can be used various methods of modifying their surface. For example, the wide-gap heterostructures can be used for these purposes with semiconductor components which have a relatively small band gap (from 2,4 eV for CdS to 1,4 eV for Bi<sub>2</sub>S<sub>3</sub>) and intensive direct transitions that allow to effectively absorb visible light in a relatively thin (several hundred nanometers) layer of photoactive substrate [3]. Thus, in the presence of S<sup>2-</sup> and at the appropriate pH, the conduction band potential of these semiconductors is more negative, than in TiO<sub>2</sub> and they can be used as photosensitizers,

to expand spectral sensitivity of TiO<sub>2</sub> electrodes, which act as effective carriers collectors. For this purpose, promising also use the mixed oxides of transition metals, such as TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>, and heterostructures BiVO<sub>4</sub>/TiO<sub>2</sub> as well. In such structures light absorption in the visible spectrum was observed, that makes them promising by using as photoelectrodes in photoelectrochemical cells [4,5]. Formation of the nanotubes layer TiO<sub>2</sub> on a titanium substrate ensures strong adhesion with layer V<sub>2</sub>O<sub>5</sub> or BiVO<sub>4</sub> and promotes the formation of a developed heterojunction surface between two types of semiconductors. Methods of obtaining such materials are different, but we stopped on electrochemical obtaining methods TiO<sub>2</sub> - V<sub>2</sub>O<sub>5</sub>, and ion layering of BiVO<sub>4</sub> films on TiO<sub>2</sub> nanotubes. These methods of obtaining films

are easy to apply and they don't need expensive equipment and reagents.

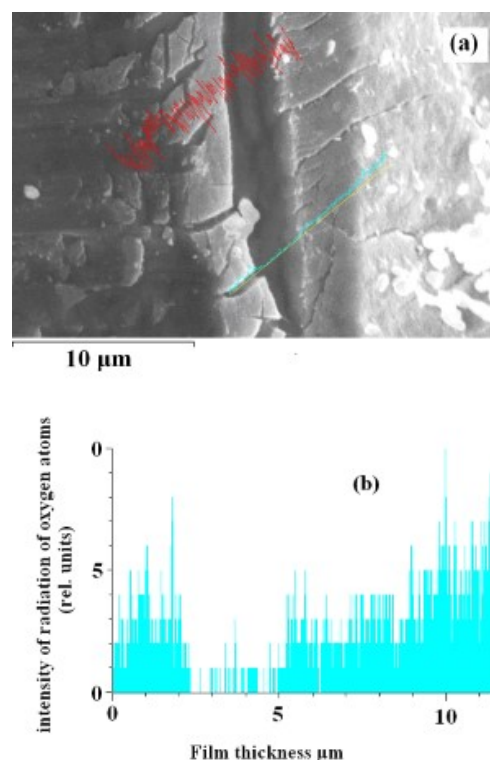
### Experimental part

By electrochemical anodization of titanium foil at a voltage of 35 V during 4 hours in a solution based on 95% glycerol and 5% solution of 0,06 M  $\text{NH}_4\text{F}$  were obtained NT- $\text{TiO}_2$  nanotubes on the surface of titanium foil. Anodic precipitation of vanadium oxide on NT- $\text{TiO}_2$  carried out in aqueous electrolyte, which contains 1 Mol/l  $\text{VOSO}_4$ , 0.1 Mol/l  $\text{Na}_2\text{SO}_4$  and 0.05 Mol/l potassium tetraoxalate. The voltage of 5 V and 0 V was changed cyclically every 3 seconds for 1 hour. Then samples were annealed at 450 °C for 3 h in air. The addition of sodium sulfate to the electrolyte reduces the anode current, probably, because of influence of the equilibrium of sulfate / bisulfate in the electrolyte [6]. Also was proposed method of co-deposition of nanotubes  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  from electrolyte, which contains 70% of glycerin, 30% of water, 1.5 mass % of  $\text{NH}_4\text{F}$  and 1 Mol / l of  $\text{VOSO}_4$ . The process was carried out by cyclic anodic polarization with a change in the voltage 24 V and 2 V every 10 sec for two hours, with subsequent annealing at 450 °C for 3 hours.

Anodizing and electrochemical measurements were performed by using potentiostat P-8s (Elins, Russia). The formation of  $\text{TiO}_2$  heterostructure with  $\text{BiVO}_4$  performed by ion layering from solutions based on 5 Mol/l  $\text{Bi}(\text{NO}_3)_3$ ; 1 Mol/l  $\text{HNO}_3$  and 5Mol/l

$\text{NH}_4\text{VO}_4$ . This films were thermally treated at 500 °C in an furnace SNOL 7,2 (Utenos, Lithuania). The measurement of optical characteristics was performed by using a spectrophotometer Perkin Elmer UV/VIS Lambda 35. Evaluation of the film thickness was performed by using of scanning electron microscopy EVO 50 XVP.

Figure 1 shows scanning electron microscopy (a) with an elemental oxygen scan by the thickness of NT- $\text{TiO}_2$  /  $\text{BiVO}_4$  film sample on the titanium substrate (b).



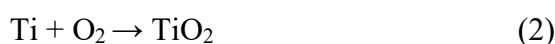
**Figure 1.** Scanning electron microscopy (a) with an elemental oxygen scan by the thickness of NT- $\text{TiO}_2$  /  $\text{BiVO}_4$  film sample on the titanium substrate (b).

In Figure 1(b) by the intensity of the oxygen atoms radiation can be estimated thickness of the oxide films.

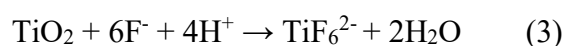
The measurement of photoelectrochemical current quantum yield ( $\eta$ ) was performed by using of a monochromator MDR-2 and xenon lamp DKSSH-500. The setup for measuring  $\eta$  and the measurement procedure are described in work [7].

### Results and discussion

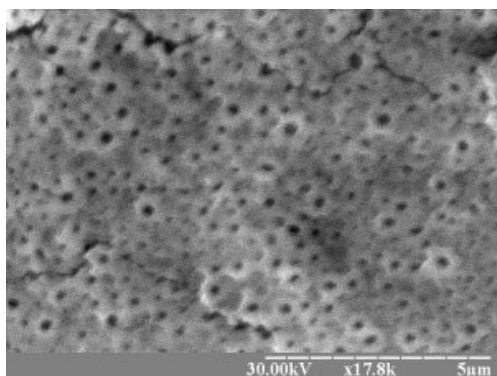
The obtaining of TiO<sub>2</sub> nanotubes by anodic oxidation of titanium can be represented as [8,9]:



The oxide film begins to dissolve with simultaneous growth, while Ti<sup>4+</sup> ions migrating from the metal to boundary of the oxide / electrolyte distribution and dissolving in the fluorine electrolyte.



The growth rate of the oxide layer at boundary of the metal / oxide distribution and the rate of oxide dissolution at boundary of pore / electrolyte bottom become equal. After that the barrier layer thickness remains unchanged, despite the fact that the process moves further into the metal, and makes pore more deep.



**Figure 1.** Electron micrograph of TiO<sub>2</sub> nanotubes

TiO<sub>2</sub> nanotubes (**Figure 2**) are wide-gap [10] and for obtaining photocurrent in the visible region of the spectrum, it is necessary to cover their surface modifying additives or semiconductors with more narrow band gap .

In connection with this, structures have been investigated with V<sub>2</sub>O<sub>5</sub> as a modifying additive and with BiVO<sub>4</sub> semiconductor layer with band gap of 2.4 eV.

A study of photoelectrochemical processes on porous TiO<sub>2</sub> films doped V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>/BiVO<sub>4</sub> heterostructures showed, that in this case the photosensitivity of TiO<sub>2</sub> to the visible region of the spectrum was observed.

Vanadium is a transition metal, and it exists in different degrees of oxidation from +2 to +5 and forms different types of oxides, formation of which depends on the temperature and pressure of oxygen [11]. A number of intermediate states are known for vanadium oxides, which represent a wide spectrum of ordered and disordered defect structures [12]. Of the large number of vanadium oxides, only a few of them are stable. In aqueous solutions, there are several types of vanadium with a degree of oxidation V<sup>4+</sup> and V<sup>5+</sup>, depending on pH and concentration, as it shown on diagram potential - pH (**Figure 3**) [13- 16].

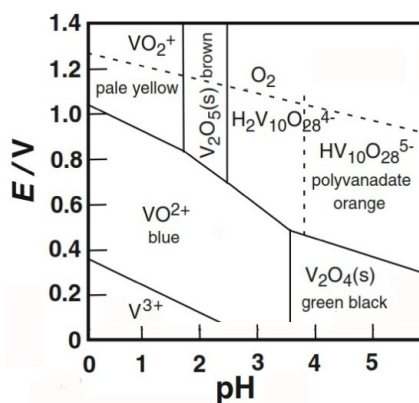
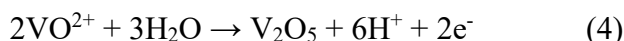


Figure 3. Pourbaix diagram of vanadium species [17].

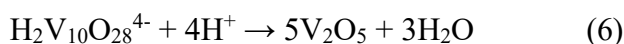
The dashed line shows the redox system  $\text{H}_2\text{O} / \text{O}_2$

As can be seen from **Figure 3**, in an acidic medium exist cations  $\text{VO}^{2+}$ . At  $\text{pH} < 4$ , soluble species  $\text{V}^{5+}$  are mainly  $\text{VO}_2^+$  and  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ . Insoluble  $\text{V}_2\text{O}_5$  appears at  $\text{pH} = 1.8$  and total concentration  $\text{V}^{5+} C = 10^{-2.63} \text{ Mol/l}$ . At different pH values, the precipitation of  $\text{V}_2\text{O}_5$  requires a higher concentration  $\text{V}^{5+}$ . For example, for  $C(\text{V}^{5+}) = 10^{-2.5} \text{ Mol/l}$ ,  $\text{V}_2\text{O}_5$  is formed between  $\text{pH} 1.68$  and  $\text{pH} 1.92$  [18].

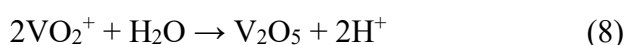
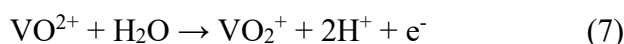
Electrodeposition  $\text{V}_2\text{O}_5$  [18] can occur either directly at  $\text{pH} = 1.8$ :



or in two phase for  $\text{pH} > 1.8$ :



and for  $\text{pH} < 1.8$ :



X-ray diffraction analysis of  $\text{TiO}_2$  film with applied  $\text{V}_2\text{O}_5$  layer (**Figure 4**) showed that two

separate phases of  $\text{V}_2\text{O}_5$  and  $\text{TiO}_2$  are formed after annealing at  $450^\circ\text{C}$ .

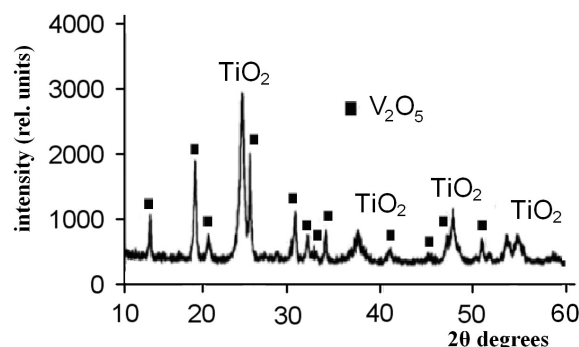


Figure 4. XRD of  $\text{TiO}_2$  with deposited layer of  $\text{V}_2\text{O}_5$  after annealing at  $450^\circ\text{C}$ .

The formation of the  $\text{BiVO}_4$  by ion layering on  $\text{TiO}_2$  nanotube surface leads to photosensibilisation of  $\text{TiO}_2$  with irradiation of visible light.

From X-ray analysis of the samples powder (scrapped off from films) (**Figure 5**) revealed, that after annealing at  $500^\circ\text{C}$  the  $\text{BiVO}_4$  monoclinic structure is formed which is sensitive to visible light at wavelengths of  $450 - 600 \text{ nm}$  [4].

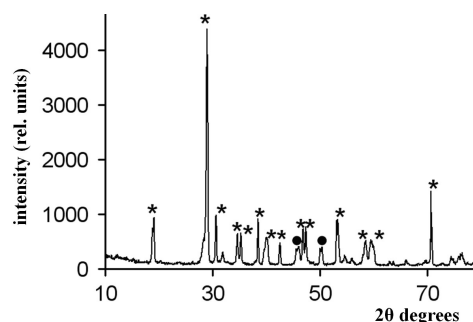
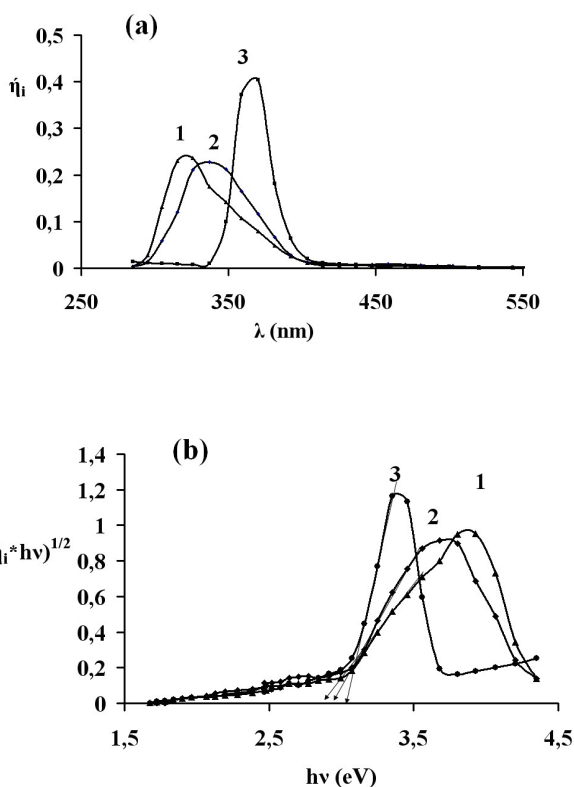
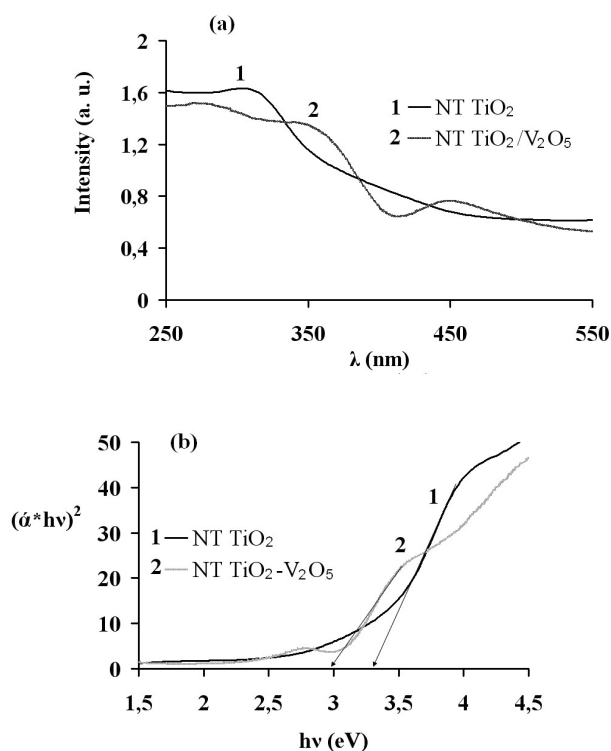


Figure 5. XRD of  $\text{BiVO}_4$  films powder treated at the temperature of  $500^\circ\text{C}$ : where \* - monoclinic  $\text{BiVO}_4$  structure, • - tetragonal  $\text{BiVO}_4$ .



**Figure 6.** The photocurrent quantum yield spectra in the coordinates  $\eta(\lambda)$  (a) and  $((\eta * hv)^{1/2})(hv)$  (b): 1– TiO<sub>2</sub>, 2– TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub>, 3 – co-deposited TiO<sub>2</sub> /V<sub>2</sub>O<sub>5</sub> (anodic deposition at potential 1.5V).



**Figure 7.** Spectral characteristics of TiO<sub>2</sub> films - 1 and TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> – 2 obtained with anodic deposition at potential 1.5V. (a) absorption spectra, (b) absorption spectra in coordinates  $(\alpha * hv)^2$  of hv.

Photosensitivity of electrodes based on TiO<sub>2</sub> / V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>/BiVO<sub>4</sub> were studied in the wavelength range 280 - 580 nm in aqueous solutions with pH = 5-7.

**Figure 6 (a)** shows the dependence of the quantum yield of the photocurrent  $\eta$  on of the wavelength NT-TiO<sub>2</sub> and NT-TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> depending on the method and conditions of obtaining at an electrode potential of 0.4 V relative to the potential of Ag-AgCl reference electrode in 1 n. KCl. It is known that  $\eta$  can be expressed in the form [19]:

$$\eta = \frac{A}{hv} (hv - E_g)^m, \quad (9)$$

where  $hv$  - photon energy,  $E_g$  – semiconductor band gap,  $m = 1/2$  for a direct transition and  $m = 2$  for indirect transition.

Bandgap TiO<sub>2</sub>, and also V<sub>2</sub>O<sub>5</sub> and BiVO<sub>4</sub>, which are the components of the films, TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> /BiVO<sub>4</sub> were determined from the dependence  $(\eta * hv)^{1/2} - f(hv)$ , and also from the dependence of the absorption coefficient in the coordinates  $(\alpha * hv)^2 - f(hv)$  for indirect-gap semiconductor, which is TiO<sub>2</sub> [20, 21].  $E_g$  value, that was calculated for TiO<sub>2</sub> electrodes, were  $\sim 3,2 \pm 0,05$  eV. However, the small thickness of the resulting thin films and defects in their structure, as a result of which a current appears in the long-wave region, does

not allow us to correctly interpret the long-wavelength edge of the photocurrent for indirect transitions [22,10]. Analysis of the absorption spectra (Figure 7 (a)) and photocurrent quantum yield (Figure 6 (a)) shows that in heterostructures NT-TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> with by the light absorption V<sub>2</sub>O<sub>5</sub> at 350 nm of the quantum yield  $\eta$  NT-TiO<sub>2</sub> increases. The figure 6 (b) shows that due to the introduction of V<sub>2</sub>O<sub>5</sub> into the structure of NT-TiO<sub>2</sub> film the photocurrent quantum yield increases. For example, in the films obtained by anodic deposition (curve 3 Figure 6 (b)) compared with other samples along with an increase in the quantum yield the band gap increases to 3.2 eV compared with TiO<sub>2</sub> where bandgap 3.0 eV (curve 1. Figure 6 (b)). An increase in the photocurrent quantum yield in the UV range may indicate a more efficient separation of the photogenerated charges as a result of V<sub>2</sub>O<sub>5</sub> action and due to the fact that vanadium oxide is deposited directly on the active centers of titanium dioxide, provides electronic contact between the components of the heterostructure and prevents recombination processes [23,24].

The decrease in photocurrent in the long-wave range of the spectrum is caused by a decrease in the absorption coefficient at the edge of the intrinsic absorption band of TiO<sub>2</sub> / V<sub>2</sub>O<sub>5</sub> at ~ 3.0 eV (Figure 7 (b)). The decrease in photocurrent in the short-wave area of the spectrum can be explained by the appearance of additional defect centers participating in the

recombination processes [7]. Comparison of the absorption spectra of NT-TiO<sub>2</sub> films and BiVO<sub>4</sub> spectra of photocurrent quantum yield Figure 8(a) and 9(a), have shown that in absorption at  $\lambda_{\text{max}} = 420\text{-}450$  nm, the peak  $\eta$  was observed, which corresponds BiVO<sub>4</sub>.

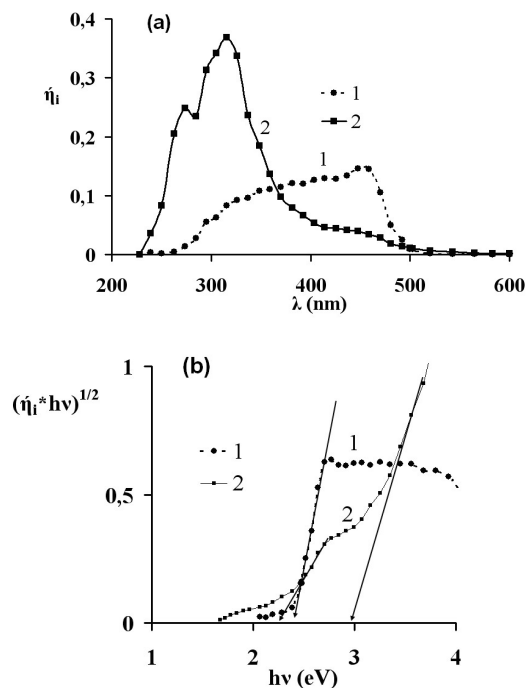
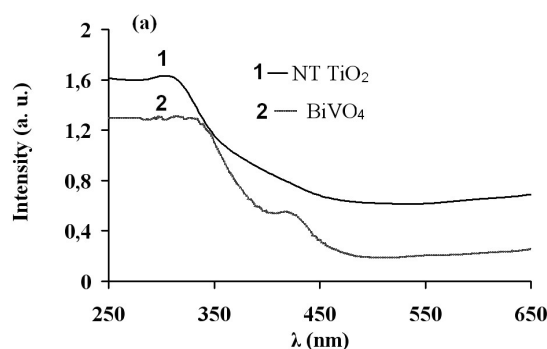
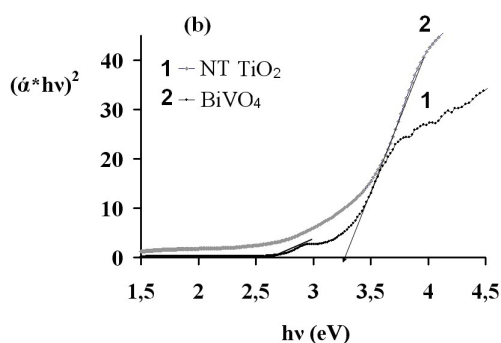


Figure 8. The spectra of photocurrent quantum yield in the coordinates  $\eta_i(\lambda)$ -(a) and  $((\eta_i * hv)^{1/2})$ -(hv) (b) for samples: TiO<sub>2</sub>(with thickness 500 nm)/ BiVO<sub>4</sub> (with thickness 2  $\mu\text{m}$ ) – 1, TiO<sub>2</sub> (with thickness 2  $\mu\text{m}$ )/ BiVO<sub>4</sub> (with thickness 2  $\mu\text{m}$ ) – 2.





**Figure 9.** The optical spectral characteristics films  $\text{TiO}_2$  - 1 and  $\text{TiO}_2$  (with thickness 500 nm)/  $\text{BiVO}_4$  (with thickness 2  $\mu\text{m}$ ) - 2 where: (a) light absorption spectra (b) light absorption spectra in coordinates  $(\alpha \cdot hv)^2$  from  $hv$ .

Analysis of spectral characteristics  $\text{BiVO}_4$  samples showed that they are characterized by indirect transitions. Dependencies quantum efficiency and absorption coefficient of the wavelength in coordinates  $(\eta_{\text{KB}} \times hv)^{1/2}$  and  $(\alpha \times hv)^2$  from  $hv$  for indirect transitions, you can estimate the width of the gap  $\text{BiVO}_4$  tangent to the x-axis on a straight section. As shown in **Figure 8 (b)** and **Figure 9 (b)** tangent to the x-axis in both cases showed that the band gap  $\text{BiVO}_4 \sim 2.5$  eV, and  $\text{NT-TiO}_2 \sim 3.0$  eV.

From the absorption and photocurrent quantum yield spectra (**Figure 8** and **Figure 9**) defined that the quantum yield of obtained heterostructures  $\text{NT-TiO}_2/\text{BiVO}_4$  and the band gap of the two components depends on the thickness of films. It was found that regulation of nanotubes thickness and  $\text{BiVO}_4$  thickness on the surface can increase the quantum yield photoelectrode in the visible spectrum. Was established, that on samples of  $\text{TiO}_2 / \text{BiVO}_4$

films with thinner layer of  $\text{NT-TiO}_2$ , observed increase in photocurrent quantum yield in the visible area of the spectrum (**Figure 8 (a)**).

By the scanning microscopy method, there was determined that the optimum thickness of  $\text{NT-TiO}_2$  films should not exceed  $\sim 600$  nm. At the thickness of  $\text{NT-TiO}_2 \sim 2$   $\mu\text{m}$  in structure  $\text{NT-TiO}_2/\text{BiVO}_4$ , as seen in **Figure 8 (a)**, quantum yield decreases in the visible area and increases in the UV light area while decreases the  $\text{BiVO}_4$  band gap to 2.3 eV (**Figure 8 (b)** curve 1). Optimal also must be  $\text{BiVO}_4$  thickness not exceeding 3  $\mu\text{m}$ . In such  $\text{BiVO}_4$  film thickness equally kept on the surface does not crack and are not showered. For example, heterostructures, where on the film  $\text{NT-TiO}_2$ , thickness 400 - 600 nm deposited  $\text{BiVO}_4$  thickness of 3  $\mu\text{m}$ , observed an increase of  $\text{BiVO}_4$  bandgap to 2.5 eV (**Figure 8 (b)** curve 2) and increase the quantum yield of photocurrent in visible range spectrum. For vanadium oxide the band gap depends on the presence in the structure of film small grain size. For the films  $\text{NT-TiO}_2 / \text{BiVO}_4$  and  $\text{NT-TiO}_2/\text{V}_2\text{O}_5$  that were obtained by chemical and electrochemical deposition, probably in the process of growing the number of small grains was increases that leading to an increase in the bandgap. So for optimal performance photoanodes based on  $\text{NT-TiO}_2 / \text{BiVO}_4$  films, can adjust their spectral characteristics by regulation the grains size.

Analysis of photoelectrochemical and optical properties of electrodes based on  $\text{TiO}_2 /$

V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> / BiVO<sub>4</sub> showed that the modifying additive slightly increases the quantum yield TiO<sub>2</sub> in the visible region. The heterostructure formation of TiO<sub>2</sub> and monoclinic BiVO<sub>4</sub> due to the correctly selected thicknesses of both layers contributes to an increase in quantum yield of photocurrent in the range of 450-480 nm to 10%

### Conclusions

Photoelectrochemical and optical studies of NT-TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> and NT-TiO<sub>2</sub>/BiVO<sub>4</sub> electrodes shows, that using simple electrochemical and chemical methods to obtain wide-gap semiconductors and doping NT-TiO<sub>2</sub> V<sub>2</sub>O<sub>5</sub> and BiVO<sub>4</sub> contributes to its photosensitivity to the visible area of the spectrum. Analysis of spectral characteristics photoelectrode showed that the ratio of the thickness of the films, obtained according to the synthesis parameters, affect on the quantum yield photocurrent. It was found that for optimal performance photoanodes based on NT-TiO<sub>2</sub> / BiVO<sub>4</sub> and NT-TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> films necessary to use NT-TiO<sub>2</sub> film thickness 600 nm doped by V<sub>2</sub>O<sub>5</sub>, and in the case of BiVO<sub>4</sub> its thickness should not exceed 2-3 μm. Under such conditions, the UV component of quantum yield photocurrent photoelectrodes decreases and contribution of visible light increases.

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