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INFLUENCE OF THE SPECIFIC SURFACE OF THE NANOSTRUCTURED TIO_2 MEMBRANE ON EFFICIENCY OF THE PHOTOVOLTAIC CELL

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Membranes of nanorods of titanium dioxide are synthesized in the work by hydrothermal method. On a surface of nanorods nanoparticles of titanium dioxide have been settled. By the nitrogen adsorption method (BET method) sizes of specific surface have been measured, full pore volume, distribution of pore by the sizes in the membranes formed by nanorods (NRs) and nanorods with the spherical nanoparticles of titanium dioxide (NRs+NPs) settled on a surface. By the method of scanning electronic microscopy morphology of a surface of the synthesized membranes has been studied. On a basis of the synthesized membranes solar cells have been collected by sensibilized dye. Volt-ampere characteristics and efficiency of cells are measured.

Keywords: titanium dioxide nanorods, solar cell efficiency, specific surface area.

Introduction

The solar power is one of the most actively developing branches of power industry now. Energy of the sun is available to everybody, is free, almost inexhaustible, and process of its transformation to electric energy doesn't exert negative impact on environment. However, today the solar power, mainly on the basis of silicon, occupies less than 1% in universal balance of the made electric power. It is connected with difficult manufacturing techniques and high cost of silicon solar elements that interferes their wide use [1].

The new generation of solar elements on the basis of oxidic semiconductors (TiO_2, ZnO, SnO) and organic materials (DSSC) has prospect of reduction in cost of the developed electric power and simplification of production. Use in sensibilized dyes solar cells of nanostructures on the basis of titanium dioxide caused a huge interest of researchers after O'Rigan and Grettsel's well-known work was published in 1991 [2]. From publications it is known that morphology, structure and design of electrodes play an important role in absorption of photons, electronic transport and efficiency [3, 4].

For receiving nanostructures on the basis of dioxide such methods as hydrothermal [5], zol-gel [6], methods of electrochemical anodizing [7] are used as a result of which structures of various morphology, such as nanoparticles, nanotubes, nanowires and nanorods are received. Use of nanoparticles of titanium dioxide is limited because of 3-dimensional electronic transport as connection between nanoparticles influences a possibility of transition of an electron from nanoparticle to nanoparticle will lead to decrease of efficiency of transport of an electron. Perspective materials for solar cells are structures with one-dimensional transport of electrons to which it is possible to carry nanotubes, nanorods and nanothreads of titanium dioxide. When using such structures one-dimensional transport of electrons along walls will be observed. It will reduce time of transfer of electrons from the centers of generation of a charge to electrodes, and also, at the correct construction of electrodes, there will be a smaller amount of the defects interfering transport of electrons [8 – 10]. Nanorods of titanium dioxide are one of perspective materials with one-dimensional transport of electrons. One of their main advantages is the possibility of synthesis of nanorods on glass with a conductor layer FTO that will allow to reduce losses on semiconductor/FTO border. Besides, nanorods possess the developed surface.

It is known that the amount of the absorbed light a photovoltaic cell directly depends on number of molecules of the dye adsorbed by a semiconductor surface. Increase in a specific surface of a semiconductor oxidic layer will allow to adsorb bigger quantity of molecules of dye and it will lead to growth of absorption of a sunlight and increase in concentration of charge carriers in a semiconductor layer.

Problem of this work is the increase in a specific surface of the membranes formed by nanorods of titanium dioxide due to modification of their surface by TiO_2 nanoparticles.

1. Experimental part

Rutile-anatase nanostructures of TiO_2 have been prepared on FTO glasses (TES-8.8 Ω/ sq.m) by means of two consecutive stages of hydrothermal synthesis. FTO of glasses were washed out by processing of ultrasound in solution of the deionized water, acetone and a 2-propanol (a volume ratio 1: 1: 1) within 30 minutes, then they were placed in a stainless steel vessel with fluoroplastic coating of 50 ml. FTO glass was established in a vessel with the carrying-out party down, in the solution containing 15 ml of the deionized water, 15 ml of hydrochloric acid (36.5-38.0%, Sigma-Aldrich), and 0,5 ml of titanium butoxide (titanium butoxide, 97%, Sigma-Aldrich). The stainless steel vessel then is closed and placed in the convective furnace at 140^0 C for 20 hours. According to the procedure described above vertical nanorods of TiO_2 were present on FTO glass. The second stage is as follows: nanorods on FTO glasses placed in the solution containing 35 ml of H_2O, 2,5 ml of sulfuric acid (36.5-38.0%, Sigma-Aldrich), and 1 ml titanium butoxide (titanium butoxide, 97%, Sigma-Aldrich) in the same stainless steel vessel with a teflon covering. The steel vessel was placed in the convective furnace at 180^0 C and maintained at this temperature during 6 hours. The received sample was washed out and dried. The sample then was calcinated at 400 ^{o} C during 2 hours.

The rutile TiO_2 nanorods received at the first stage of hydrothermal synthesis subjected to water processing of $TiCl_4$ (0.4 M $TiCl_4$ during 1 hour at ambient temperature) [11,12].

The morphology of a surface and cross cut of samples have been received on the scanning electronic microscope MIRA 3LMU (Tescan, the Czech Republic).

Measurement of a specific surface was taken by BET method, distribution of the size of pores, dependence of pores volume on their diameter have been received from isotherms of adsorption and a desorption of nitrogen on the measuring complex Sorbi-MS (Russia). Thermal training of samples was carried out at a temperature of 100^0C within 180 minutes in the block of prepreparation "SorbiPrep".

In organic solar cells dye is one of key components. Efficiency of cells depends on its absorptive capacity, concentration. We used N719 (Sigma-Aldrich) dye which is characterized by a high absorptive capacity and is often used in the photovoltaic cells. Sorption of dye was carried out from ethanolic solution with concentration 10^{-4} mol/l during 18 hours. As electrolyte in a cell Iodolyte H30 was used (Solaronix, Switzerland). As laying between a working electrode and an electrode of yield in a solar cell served the membrane, in thickness of 25 microns the Meltonix brand (Solaronix, Switzerland).

Volt-ampere characteristics were measured in the standardized conditions at radiation by light of a source with the range imitating solar (Air Mass (AM) 1.5). Standard power of a source made 100 mW/cm^2 (PET PHOTO Emission TECH., INC.).

EIS measurements were taken under the standard feigned sunlight of AM 1.5, 100 of mV/cm2 (PET PHOTO Emission TECH., INC.) on an impedancemetre Z–500PRO (Elins), amplitude and range of frequency of the enclosed sinusoidal signal – 15 mV and 500 kHz-100 kHz respectively.

2. Results and discussion

Morphology of the membrane surface from nanorods of titanium dioxide received on the scanning electronic microscope is presented in figure 1.

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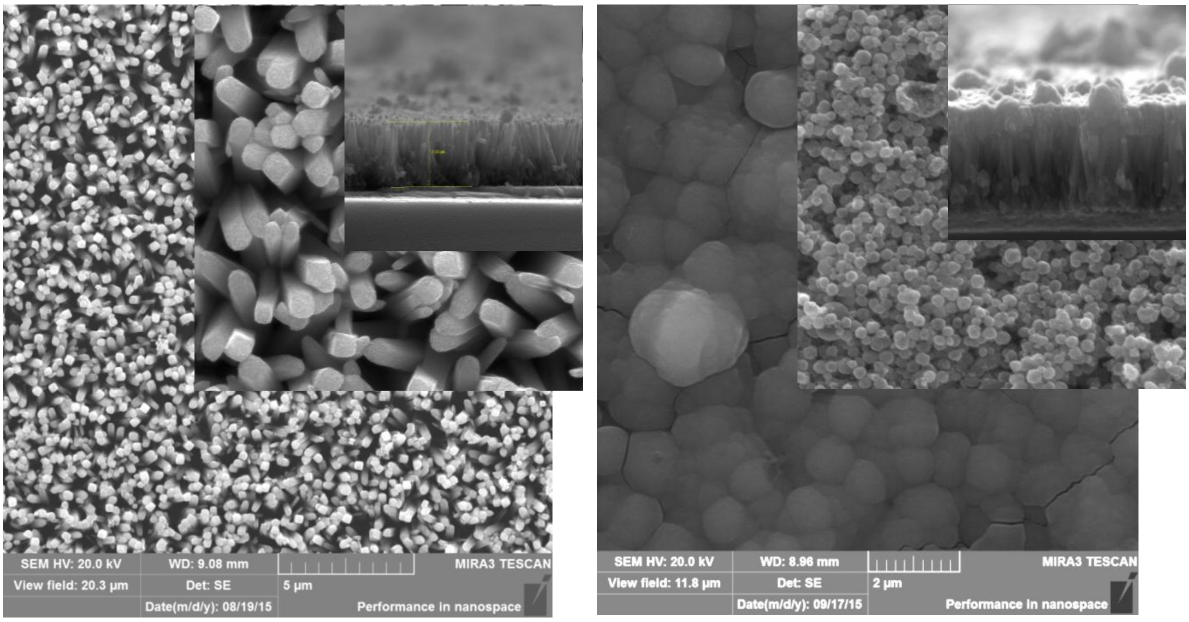

a) b)

Fig.1. Nanorods of titanium dioxide after the first stage; nanorods of titanium dioxide on surface of which nanoparticles of titanium dioxide at the second stage are settled (b)

In a picture it is visible (figure 1, a) that on a surface of FTO glass the nanorods of titanium dioxide located perpendicularly to the substrate plane are formed. Average diameter of nanorods after the first stage of synthesis makes 100-120 nanometers, and length is 3.5 microns. At the second stage on a surface of the nanorods received at the first stage spherical nanoparticles TiO_2, with an average diameter of 200-250 nanometers have been settled (figure 1, b). Total thickness of membrane has made 4 microns.

For measurement of a specific surface, the membranes have been separated from glass and are placed in an adsorber. Measurement was taken at a temperature of liquid nitrogen. For release of a surface from moisture samples during 180 minutes were calcinated and blown at a temperature of 100 ^{0}C. Results of measurements are given in table 1.

Table 1 - Specific surface of samples after the first and second stage

№	Specific surface area, S_{BET}, м^2/g	Full pore volume, Vp, см^3/g
TiO_2 NRs	29	0.042
TiO_2 NRs+NPs	38	0.061

As it is seen from table 1, application of nanoparticles of titanium dioxide on a surface of nanorods leads to increase of specific surface and total pore volume. Small increase of Sуд can be explained with the fact that nanoparticles possess more developed surface, than nanorods.

Measurement results of isotherms of nitrogen adsorption and desorption are given in figure 2. From the figure it is seen that in initial part isotherms have the convex form that demonstrates strong interaction of an adsorbate with adsorbent. At increase in pressure to P/P_0=1, the isotherm asymptotically approaches a straight line. Then the volume of the adsorbed gas increases in area 0.8 to 1. The received isotherms belong to the II type of adsorption which corresponds to polymolecular adsorption, similar results for titanium dioxide have been received in work [13]. Basing on results of the measured isotherms distribution of pores on a surface of sample which is shown in figure 3 has been calculated.

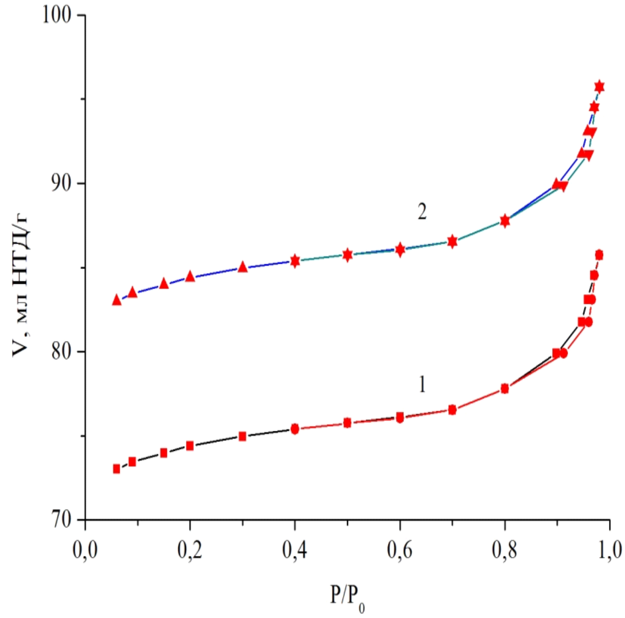

Fig.2. An isotherm of nitrogen adsorption and desorption on a surface of membranes:
1 – after the first stage, 2 after the second stage

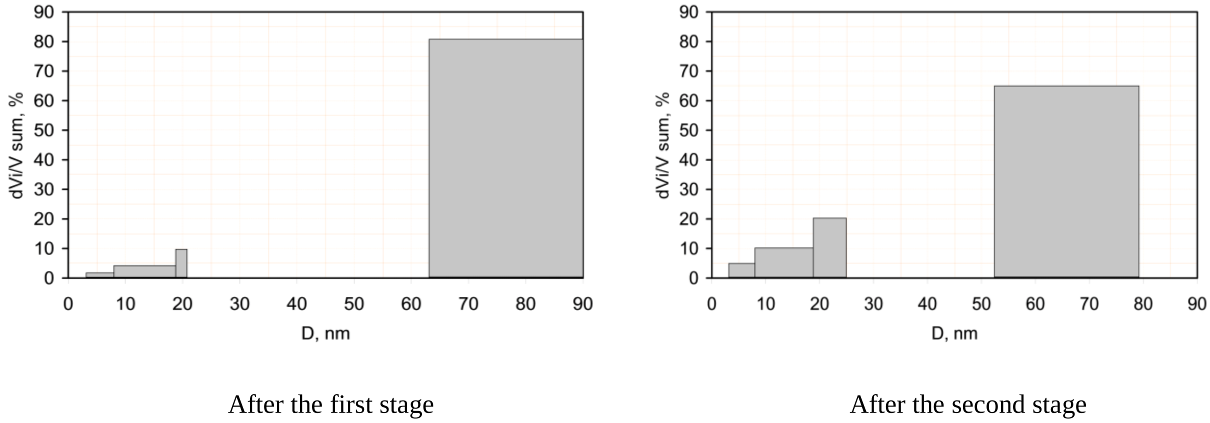

Fig.3. Distribution of pores concerning their total amount

From the figure it is seen that after the first stage of hydrothermal synthesis at a surface of membrane there are pores of various diameter. Pores up to 20 nanometers takes about 15% of all pore volume, and pores from 65 nanometers to 90 nanometers about 85%. At modification of a surface of nanorods of titanium dioxide nanoparticles, also distribution of pores of rather total amount changes. Pores from 5 to 25 nanometers occupy 35%, and pores from 50 to 80 nanometers - 65%.

Curves of volt-ampere characteristics are given in figure 4.

As it is seen from the figure, at addition of nanoparticles in structure of nanorods of titanium dioxide current density of short circuit has increased by 2,5 times. DSSC on the basis of the massif of nanorods and nanoparticles has shown the greatest efficiency of transformation of solar energy to electric. The more the specific surface area, the more amount of dye can be on the single area of a substrate. Therefore, bigger quantity of electrons are injected under the influence of sunlight that increases cell current. The main indicators of solar cells received as a result of measurement VAC are given in table 2.

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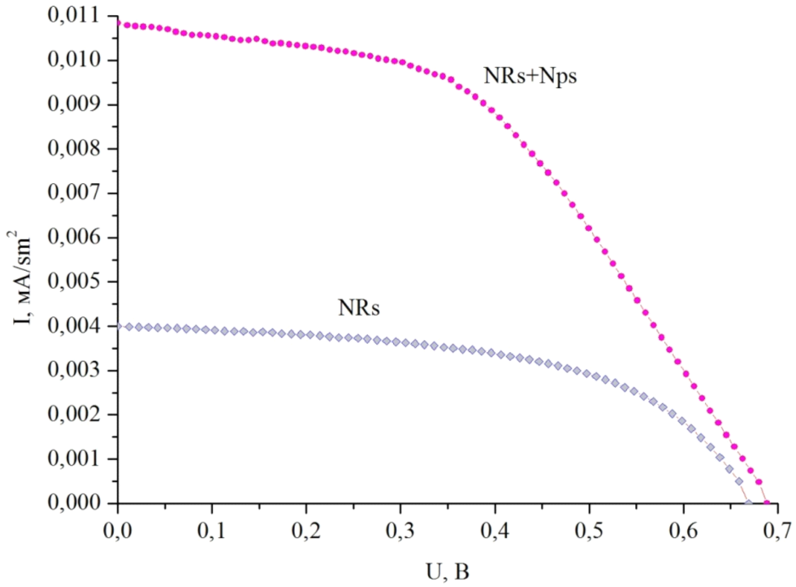

Fig.4. Volt-ampere characteristics of solar cells

Table 2 - Photo-electric characteristics of solar cells

No.	Specific surface area, S_{BET}, m^2/g	Open circuit voltage, $V_{oc,}$	Short-circuit current Jsc (mA/cm^2)	Fill factor, FF	R_s, Om	R_{sh}, Om	Efficiency η, %
NRs	29	0.66	0.004	0.54	265	3875	1.43
NRs+NPs	38	0.68	0.01	0.47	122	2839	3.56

From tabular data it is seen that in the result of modification of a surface of nanorods resistance is decreased by the nanoparticles of titanium dioxide R_s. For a real solar element resistance R_S consists of consistently included resistance, which are responsible for quality of contact layers, and R resistance (leak resistance which in ideal SE is supposed to be infinitely big) reflects possible channels of current leakage. That is, in the ideal solar element $R_s \to 0$, a $R \to \infty$.

The analysis of data of table 2 shows that at modification of a surface of nanorods spherical nanoparticles along with current growth of short circuit the size R_s falls that demonstrates improvement of ohmic contact in membrane. At the same time modification of a surface of nanorods - to falling of size of the shunting resistance. In general, the efficiency of solar cells on the basis of “nanorods-nanoparticles” system TiO_2 increases in comparison with cells on the basis of nanorods.

One of the most widely used methods at research of electrophysical characteristics of solar cells is measurement of an electric impedance [14]. The essence of the method consists in influence by a signal in the form of sinusoidal wave and supervision over behavior of system in response to this indignation. Impedansogram of cells on the basis of porous membranes TiO_2, received at different stages of synthesis, are given in figure 5.

On the basis of the received ranges of an impedance and the technique described in work [15] for cells the effective coefficient of diffusion of electrons D_{eff}, effective speed of recombination k_{eff}, effective time of life of an electron τ_{eff}, resistance of electronic transport in membrane of titanium dioxide R_w, resistance of transfer of a charge connected with recombination of an electron R_k, *Con* defined as $Con = R_k L k_{eff}$ have been calculated. The received results are given in table 3.

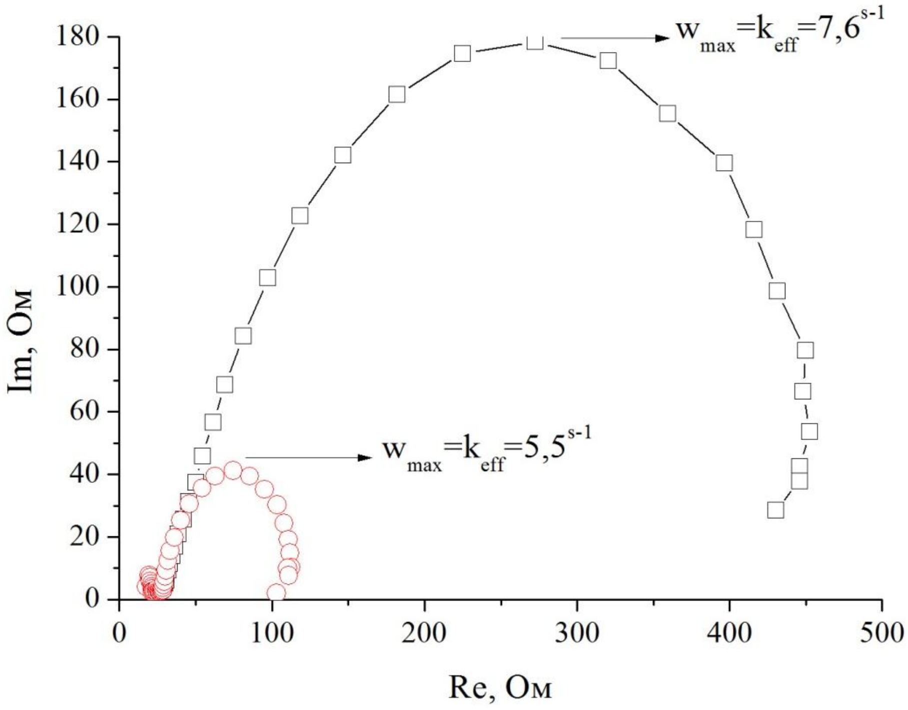

Fig.5. Impedansogram of a cell

Table 3 - Electrophysical characteristics of the cells received at different stages of synthesis

Sample	D_{eff} ($cm^2\ s^{-1}$)	k_{eff} (s^{-1})	τ_{eff} (s)	R_k (Om)	R_w (Om)	Con (Om cm s^{-1})	L, mkm
TiO_2 NRs	$12*10^{-5}$	7.6	0.13	413	13.7	1.09	3.5
TiO_2 NRs+NPs	$26*10^{-6}$	5.5	0.18	92	3,06	0.2	4

Speed of recombination k_{eff} is determined by peak frequency ω_{max} of the central arch (in the range 500 kHz-100 MHz) $\omega_{\max} = k_{eff}$, R_k, is determined by diameter of the central arch, R_k/R_w is defined from a form of the central arch. When the arch is the correct circle, R_k is much more than R_w. The effective coefficient of electrons diffusion D_{eff} is defined as follows:

$$D_{eff} = \left(\frac{R_k}{R_W} \right) L^2 k_{eff}$$

From table 3 it is seen that the cell on the basis of nanorods and nanoparticles of titanium dioxide received after the second stage of synthesis possesses the best electro transport properties. The minimum value of resistance of electronic transport in TiO_2, the low speed of recombination and longer effective time of life of an electron is observed for it.

Conclusion

Thus, in the result of hydrothermal synthesis the massifs of nanorods of titanium dioxide sent perpendicularly to the substrate plane are synthesized. On the received nanorods spherical nanoparticles of titanium dioxide have been settled. Sizes of a specific surface and pore volume of

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membranes have been compared. It is established that at settlement of nanoparticles of titanium dioxide on the surface of nanorods TiO_2 the specific surface and pore volume increases. By measurements of volt-ampere characteristics it is established that current density grows, the factor of filling and efficiency of solar cells increases. At modification of a surface of nanorods TiO_2 nanoparticles R_s resistance, responsible for quality of interlaminar contacts decreases. At that time channels of current leakage increase. As a result of measurement of an impedance of a range it is established that the cell on the basis of nanorods and nanoparticles of titanium dioxide received at the second stage of synthesis possesses the best electro-transport properties.

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