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Electromotive Forces in Solar Energy and Photocatalysis (Photo Electromotive Forces)

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1. Introduction

The photoelectric polarization method is based on the inner photoeffect phenomenon which can be observed upon illumination of a photoactive material. Upon illumination of an oxide in its own region of optical absorption the arising non-equilibrium electrons and holes can be spatially separated within the surface oxide phase in a way when on one of interface boundaries there appears an excess of nonequilibrium negative charges, and on the other – an excess of positive charges. The photoelectric polarization emf arising as a result of charge carrier separation can be measured. Thus, the inner photoeffect is a structure-sensitive property of compounds. The inner photoelectric effect is of interest, on the one hand, as a factor that is responsible for a number of electrochemical and corrosion effects arising upon the exposure of metal and semiconductor electrodes to irradiation. On the other hand, it can be used for obtaining information on the nature and character of processes proceeding on the real materials. Thus, this method can be widely used for the evaluation of photoactivity of modern solar elements and photochemical converters of solar energy. The pathways for charge collection are much shorter, allowing the use of inexpensive low-quality materials, and also of organic semiconductors in which light absorption generates not free charge carriers but short-lived excitons that must reach an interface in order to separate at it and generate photocurrent and photo-emf. Thus, in this chapter we will consider the principles and peculiarities of the arising of the photo-emf in porous nanoarranged coatings using the most practiced synthesis methods: sol-gel method, polymer-assisted synthesis and electrochemical precipitation. At the same time, photocatalysis is closely related to photoelectrochemistry, and the fundamentals of both disciplines are covered in this volume, as among the key objects described there have been chosen the films on the basis of nanostructured titania that is widely used both as a catalyst and a component of solar elements. Finally, we will describe the measurement of electron-transfer dynamics at the molecule/semiconductor interface, and cover techniques for the characterization of photoelectrochemical titania-based systems.

2. Fundamentals in photoelectrochemistry

Titania-based preparations occupy nowadays leading positions both in the field of industrial photocatalyst manufacturing (Hombikat, Degussa P-25, P-90, etc.), and in the sphere of scientific studying. The basic direction of researches is the determination of approaches to increasing the photoactivity [Vinogradov et al., 2008, 2009, 2010]. Thus quantization effects play decisive role in the processes of generating the electron-hole pairs. Nanosized TiO_2 particles are of outstanding importance in this context. When electrons and holes are confined by potential barriers to small regions of space where the dimensions of the confinement are less than the de Broglie wavelength of these charge carriers, pronounced quantization effects develop; the length scale below which strong quantization effects begin to occur ranges from about 5 nm to 25 nm for typical semiconductors.

Among the most widespread methods of obtaining the colloidal semi-conductor nanoparticles the sol-gel technology occupies leading position. In the papers by Agafonov et al., there was shown a manifestation for high photoactivity of nanodisperse TiO_2 particles obtained by titanium isopropylate hydrolysis, which was estimated using data of photopolarization measurements. The use of the given technique allowed to achieve both optimum parameters for comparison of photoactivity of synthesized preparations, and the deepest interpretation of studied properties.

The main factor that determines unique photoactivity properties of titania-based materials is the dispersion of used preparations. Using semiconductor particles in the process of photocatalytic reactions is possible only in the case of the presence of a highly developed surface, under conditions of separating the formed electron-hole pairs without recombination at their movement from bulk to surface. Besides, the more developed a surface is, the more difficult it is for carriers to unite again. At the same time oxidation and reduction reactions should take place simultaneously on a particle surface (otherwise the particle will be charged, and the reaction will stop). The limiting stage will therefore be the rate of chemical reaction. Thus, the particle acts as a microelectrode, keeping the potential of anodic and cathodic electric currents that are equal in magnitude. When using large semiconductor particles, currents formed in them have insignificant magnitude in the darkness under open chain conditions as the basic density of charge carriers (for example, electrons in an n-type semiconductor) on a surface will be minimal because of long distances of movement, as is shown in $d \ll d_{sc}$, where d_{sc} is a thickness of charge transfer area. At the same time, in the case of very small sizes of particles there takes place a reverse procedure, because there is not enough room for formation of charges in the bulk, $d \ll d_{sc}$. After a slight light excitation, insignificant charge carriers (for example, holes in n-type semiconductors) in the largest particles become electron donors in solutions, and it leads to a negative charge of the particle and provides a positive charge of the entire complex. Thus, the combination of these two processes leads to the mutual leveling in the energy of the entire system.

In a semiconductor with small particles ($d \ll d_{sc}$), the photogenerated electrons and holes can easily move to the surface and react with electrons and holes of acceptors, provided that energetic leveling is observed.

3. New inorganic materials – perspective for solar energy conversion

While science development stimulated essential interest in the field of photo- and electrochemistry, considerable progresses in the increase in sensitivity and depreciation of

solar elements on the basis of solid-state photogalvanic cells have been made. Thus, the understanding of such a progress can be reached if we consider the basic fundamental concepts. Using solid-state cells demands direct contact between two phases of substances with different mechanisms of conductivity. Metal-semiconductor contact can be provided by a Schottky barrier while semi-conductor layers with different polarity of carriers provide p-n type. Excitation of an electron-hole pair as a result of a photon absorption by the semiconductor is possible in such systems if an energy of a photon is more than the bandgap ($h\nu > E_g$). In this case, charge carriers at the interface can be separated effectively into separate electrons and holes, and that in turn increases the currents in the external contour. In such materials the conductivity of solid-state particles is electronic as a rule. Intensive researches during the last two decades have led to the inevitable conclusion that a rather narrow bandgap promoting phototransformation of visible light is peculiar for preparations with weaker chemical bond in the semiconductor, and that leads to the processes of self-oxidation and photocorrosion, which destroys used materials. The solution of this problem is probable by monitoring the separation of light absorption and charge separation functions, by sub-bandgap sensitization of the semiconductor with an electroactive dye. A wide bandgap is peculiar for a stable semiconductor, such as titanium dioxide with $E_g = 3.1$ eV, which therefore normally exhibits a photovoltaic response only under ultraviolet irradiation, can then photorespond to visible light of wavelength 400 – 750 nm, or 1.6 – 3.0 eV photons.

Impurity-induced conductance changes are therefore often much smaller than expected. In fact, in many 'doped' nanoporous films, the observed conductivity is found to be due to a hopping-type defect conduction mechanism, and may therefore be of only limited use in devices. The top-view image (Figure 1a) is coherent with disordered crystalline nanoparticles with narrow particle size distribution, approximately 10 nm. According to the general diffraction data (Figure 1b), the material is constructed from the anatase-brookite form crystallites, with size of about 5 nm (according to ring broadening). According to the low-temperature nitrogen adsorption – desorption data (Nova 1200e), the specific surface area of such a material amounts to 162 m²/g, fig. 1c.

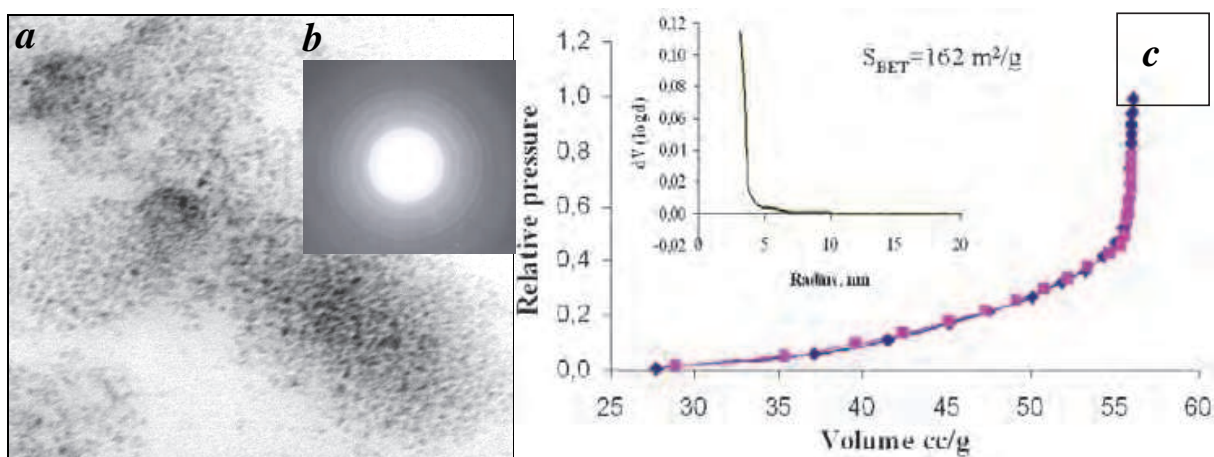


Fig. 1. The TEM images of titania film without silver nanoparticles: a) top-view; b) electron transmission diffraction pattern; c) adsorption – desorption isotherms of nitrogen and pore size distribution.

Figure 2a shows AFM micrographs of porous nanocrystalline anatase TiO_2 films with a grain size of approximately 10 nm. The volume fraction in these films is about 50% and measurements by the BET method show that the internal surface area is several hundred times the planar area for a 5 thick film.

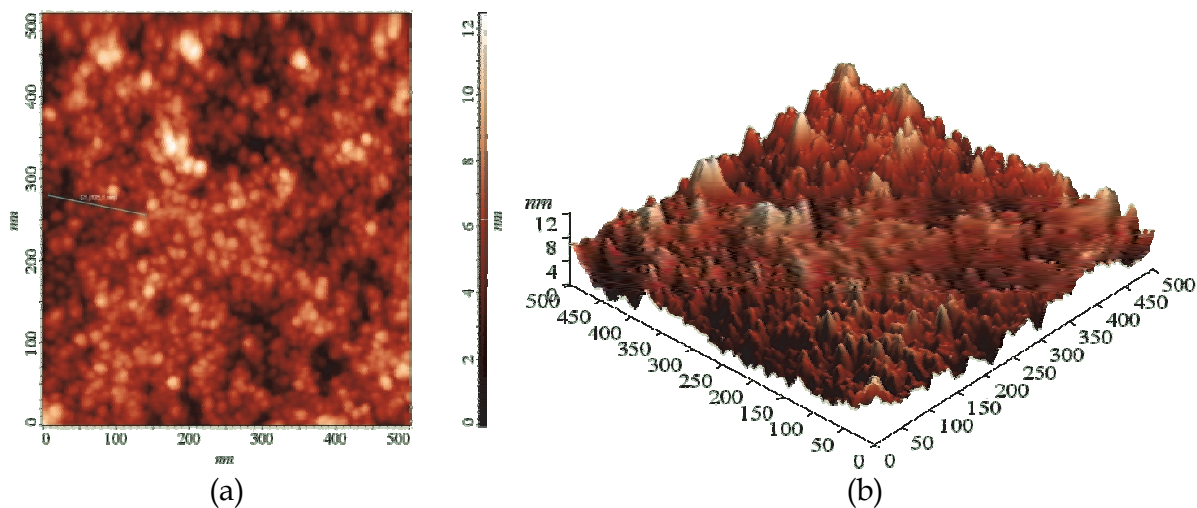


Fig. 2. (a) The AFM micrograph of nanoporous TiO_2 film formed by spherical nanoparticles with narrow size distribution.

4. Method of photoelectric polarization

The essence of the photoelectric effect is as follows: when light of the corresponding wavelength and energy is absorbed by a crystal, from its surface electrons are emitted. Action of usual photocells is based on this principle. If a material is in vacuum, then it appears possible to collect emitted electrons, applying certain voltage. The resulting current force is the measure for quantity of absorbed light.

In the second half of the 20th century Russian scientists E.K.Osche and I.L.Rosenfeld suggested using the method of measuring the photoelectric polarization for determining the kinetics of electrode reactions occurring upon anodic oxidation and metal passivation, and also for estimating the structural and semiconductor properties of metals. Oxides on the surface of metals are compounds of variable composition for which the deviation from stoichiometry is the main and natural property. Thus, depending on character of such a deviation, i.e. on whether excess metal or oxygen prevails in the lattice, an oxide can possess electronic or hole type of conductivity. Degree of the deviation from stoichiometry, i.e. how much concentration of one of the excess components exceeds another, determines the concentration of free charge carriers in an oxide [Osche et al., 1969].

The internal photoelectric effect is of interest, on the one hand, as the factor responsible for a number of electrochemical and corrosion effects arising upon irradiation of metal and semiconductor electrodes. On the other hand, it can be used in structurally-sensitive photoelectric methods for obtaining information on the nature and character of the processes occurring on the real electrodes [Osche et al., 1978].

5. Technique of measuring the photoelectric polarization

The PEP method is based on the phenomenon of internal photoeffect observed upon illumination of an electrode placed in an electrolyte. Under the influence of light, in the

surface layer there arise electron-hole pairs which are spatially separated in the electric field of impoverished layer: the electrons move deep into the semiconductor, and the holes close to the surface, reducing the magnitude of the surface charge. The bulk spatial charge is formed, therefore from the direction of irradiated contact the Schottky barrier magnitude decreases, and the height of the second barrier does not change. Simultaneously the electrons grabbed by the adsorbed oxygen atoms on the surface are released and move towards the conductivity zone, and the holes move to the valence zone, thereby reducing barriers on boundaries between particles. Because of the decrease in barrier, on the electrodes there arises a potential difference that is equal to the observed photo-emf, and the electrons from near-contact areas tunnel into the semiconductor, thereby generating a photocurrent [Vakalov et al. 2010].

The block diagram of installation for measuring the photo-emf is shown in Fig. 3. The photo-emf measurements are carried out in the usual electrochemical cell 1, in which except the electrode under study 2 the auxiliary electrode of the platinized platinum 3 is placed. Illumination of an investigated electrode is performed by rectangular impulses of non-spread light of a mercury lamp 7 through the quartz lens 6 and the quartz glass 4. The quartz lamp is turned on using the incendiary device 9. Duration of a light impulse is set by means of the photoshutter 5 and amounts to $5 \cdot 10^{-3}$ s. For the registration of the photo-emf arising in the surface layer upon pulse illumination, there serves the oscillograph 11, on the screen of which the sign and amplitude of the photoresponse are observed. The photoelectric signals from the cell are amplified using the amplifier 10. Wires in the alternating voltage chain should be contained in a metal braid and have the minimum length. While these conditions are observed allowing to reduce the level of the extraneous noise to a minimum, the registering scheme provides sensitivity to $5 \cdot 10^{-6}$ V.

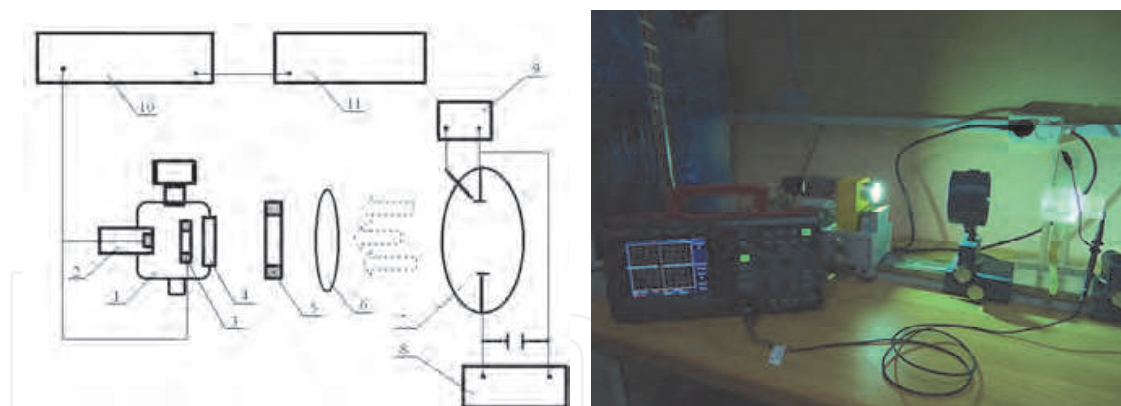


Fig. 3. The scheme of installation for measuring the photoelectric polarization: 1 – cell; 2 – working electrode; 3 – auxiliary electrode; 4 – quartz glass; 5 – photoshutter; 6 – quartz lens; 7 – DRS-250 mercury lamp; 8 – VSA power source; 9 – lamp incendiary device; 10 – amplifier UC-28, 11 – oscillograph S1-69.

6. Interpretation of data on the photoresponse arising in nanomaterials

The internal photoeffect belongs to structurally sensitive properties of a crystal. Therefore there is a basic possibility of using the internal photoeffect for obtaining the information on defective structure of an oxide, in particular, on the character and degree of deviation from stoichiometry. The surface oxide on metals is as a rule accepted to have the constant

composition corresponding to the stoichiometric formula of compounds. Meanwhile, metal oxides are compounds of variable composition, for which the deviation from stoichiometry is thermodynamically caused phenomenon. Depending on the surrounding conditions (pressure of oxygen, temperature) such compounds are capable to change the ratio of excess metal and oxygen in their crystal lattices within the considerable bounds without formation of a new phase. So, for example, the titania phase, whose deviation from stoichiometry is caused by the loss of balance of anionic and cationic vacancies, remains stable in the range of structures $\text{TiO}_{1.35}$ – $\text{TiO}_{0.69}$. The other oxides suppose much less deviations from stoichiometry without formation of a new phase. Such compounds, depending on the character of deviation from stoichiometry, can possess n- or p- conductivity type. Degree of deviation from stoichiometry determines the concentration of own nuclear defects and of free charge carriers in an oxide, charge and substance transport and reactivity of an oxide. The most insignificant deviations from stoichiometry lead to a sharp change in physical and chemical properties of an oxide. For example, electrical conductivity of stoichiometric oxide TiO_2 is $10^{-10} \text{ Om}^{-1} \text{ cm}^{-1}$, and that of non-stoichiometric one $\text{TiO}_{1.9995}$ is $10^{-1} \text{ Om}^{-1} \text{ cm}^{-1}$. The calculation of the metal surface oxide composition degree of deviation from stoichiometry on the basis of measurements of photoelectric polarization is performed in [Osche et al., 1978]. For the calculation of the stationary electromotive force of photoelectric polarization let us write down the concentrations of darkening electrons and holes as follows:

$$p_0 = N_B \cdot \exp(E_B - F_0), \quad (1)$$

$$n_0 = N_C \cdot \exp[-(E_C - F_0)], \quad (2)$$

where N_B and N_C is the density of states in valence and free zones; E_B is the energy of an upper part of the valence zone; E_C is the energy of a bottom part of free zone; F_0 is a Fermi's level.

By analogy, for non-equilibrium holes and electrons it is possible to write down:

$$p = N_B \cdot \exp(E_B - F_p), \quad (3)$$

$$n = N_C \cdot \exp[-(E_C - F_n)], \quad (4)$$

where F_p and F_n is a hole and an electron Fermi quasilevel.

From the equation system (4, 5) we have:

$$\ln \frac{p_0}{n_0} = \ln \frac{N_B}{N_C} + (E_B - F_0) + (E_C - F_0).$$

By analogy, for the equation system (3, 4) we have:

$$\ln \frac{p}{n} = \ln \frac{N_B}{N_C} + (E_B - F_p) + (E_C - F_n).$$

Thus, the stationary EMF of photoelectric polarization arising upon illumination is equal to:

$$V_{PEP} = \ln \frac{p}{n} - \ln \frac{p_0}{n_0} = (F_n - F_0) - (F_0 - F_p) \quad (5)$$

or in Volts:

$$V_{PEP} = \frac{k \cdot T}{e} \cdot \left(\ln \frac{p}{n} - \ln \frac{p_0}{n_0} \right). \quad (6)$$

7. Photoresponse in TiO₂-based nanomaterials obtained using different methods

Photoelectrical properties of wide bandgap metal oxide (TiO₂, ZnO, etc.) thin films have drawn a great deal of attention in recent years due to their wide application in solar cells and photocatalysts [Gratzel et al., 1991; Masakazu, 2000]. Titanium dioxide is one of the promising candidates in the dye-sensitized [Li et al., 1999], conjugated polymer [Kwong et al., 2004] and inorganic semiconductor [Rincon et al., 2001] based solar cell applications. Presently many research groups are involved in improving the photoconduction and photovoltaic efficiency of the TiO₂ thin films by enhancing the charge carrier transport and by reducing the recombination centers. Titanium dioxide exhibits polymorphs such as anatase, rutile and brookite. Among the above structures, anatase exhibits higher photoactivity than rutile and brookite. Usually as deposited TiO₂ thin films are amorphous and photoinactive in nature. To achieve the photoactivity in these films structural transformation from amorphous to anatase phase is necessary. Thermoannealing is one of the suitable post-treatments to attain the phase transformation from amorphous to crystalline structure. During the thermoannealing processes the oxidation state of 2pO valence bands is modified due to the energy contribution from anharmonic electron-phonon interaction [Kityk et al., 2001] and it leads to reduction of Ti⁴⁺ states to Ti³⁺ states. Moreover, the critical energy necessary for such process even given by IR induced principle corresponds to about 420°C [Kityk et al., 2005], which is confirmed in the present work by photo transient decay spectra of TiO₂ films annealed at 425°C. Creation of this oxygen vacancies (Ti³⁺) act as a trap levels in TiO₂ layers and it influences the efficiency of the dye-sensitized solar cells [Weidmann et al., 1998]. The knowledge of the trap levels and study of their nature will lead to understand the efficiency limiting parameters in the solar cells. Thermally stimulated current (TSC) measurement is a well-known non-isothermal technique for the investigation of trap levels in semiconducting materials [Zeenath et al., 2000; Pai et al., 2007]. This permits to determine the gap states and their capture cross section. The study of photo transient decay provides an understanding of photogenerations and transport of free carriers in the solid.

However, recent publications on obtaining the photoactive titania of anatase-brookite crystal form from a solution by using temperature dehydration [Alphonse et al., 2010] have allowed to essentially expand the spectrum of using titania in combination with organic sensitizers and metal nanoparticles while creating solar cells. Thus, in this chapter of the monograph we will consider the basic approaches on the establishment of the reasons of photo-emf emergence in the thin TiO₂ films obtained using the most widely used and modern methods, such as template synthesis, sol-gel technology with ultrasonic treatment, anodic electrochemical precipitation, precipitation of the layered heterostructures containing metal nanoparticles or organic dyes.

8. Sol-gel technology employing ultrasonic treatment

As a basic method of sol-gel synthesis we have used an approach, in which stabilization of hydrolysis process was performed by regulation of pH with formation of colloidal nanocluster system, which can develop into gel (pH 2–6, formation of macroscopically oriented structures) or sol (pH > 6, nanosized metal-polymer complexes). Modifying was performed using sonochemical treatment. Sol formation took place upon thermal treatment at 80°C. Further calcination led to the formation of crystallized nanoparticles, see Fig. 4.

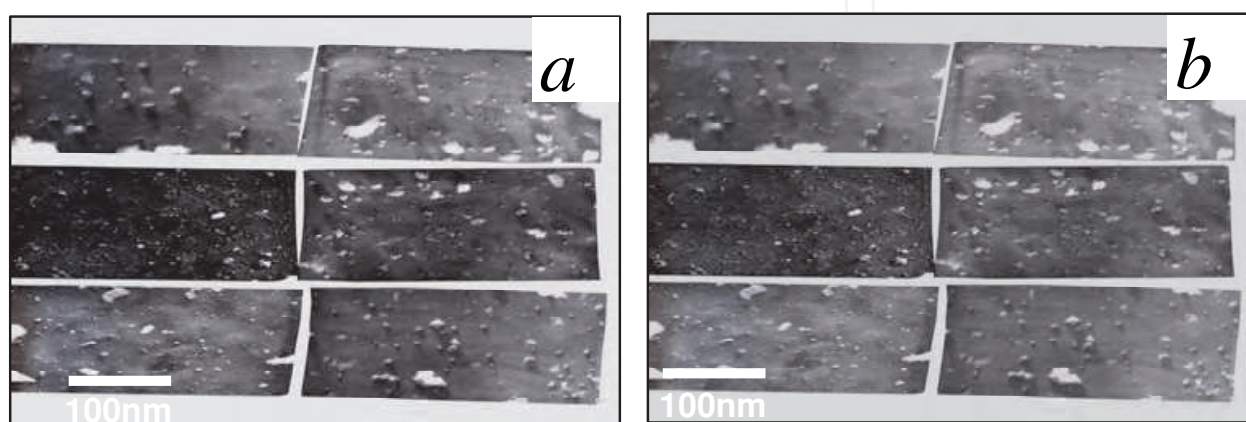


Fig. 4. The TEM images of titania powders, prepared a) with USI and diethylamine, b) with USI and acetic acid.

As investigations have revealed, using ultrasonic treatment, it is possible to substantially increase the photoactivity of synthesized preparations. The reason for this is correlation of the structure formed upon intensification of olation and oxolation processes, which in turn promotes obtaining highly stable sols that form defectless nanocrystals, as a rule, in anatase form. Absence of the stage of thermal treatment in the given synthesis method results, according to X-ray analysis data, in an amorphous phase. Calcination of films led to an increase in photo-emf by ten or more times, that is related to the formation of crystal phase. Using diethylamine as the initiator of hydrolysis as compared to ice acetic acid promotes sharp increase in the photoresponse indices and increase in crystal density. For a film obtained using diethylamine this index was 22 mV, and using ice acetic acid – 8 mV, Table 1. Such a substantial increase can be caused by a decrease in deficiency of crystals as ultrasonic modifying promotes formation of dense crystal package. Recombination of photoelectrons and holes, apparently, is the main reason of a decrease in photocatalytic activity of the materials obtained without ultrasonic treatment. Emergence of p-type conductivity, apparently, is determined by non-stoichiometry and occurrence of discrete levels in the bandgap because of an excess of acceptor impurities in the built crystal lattices formed as a result of formation of hybrid compounds. Table 2 summarizes the results of comparative characteristics of the photoresponse films.

Material designation	Polarity of conductivity	Electrode	Photo EMF, mV	Average crystallite size, nm
TiO ₂ , pH=4	P-	Ni	1.5	7.5
TiO ₂ , pH=11	P-	Ni	6.8	6
TiO ₂ + USI, pH=4	P-	Ni	8.0	9
TiO ₂ + USI, pH=11	P-	Ni	22.0	8.1

Table 1. The response of photoelectromotive force.

9. Anodic oxidation

As compared to the other methods of obtaining the corresponding oxides on the metal surface (thermal, chemical oxidizing), electrochemical oxidation has a number of advantages. In particular, anodic oxidation is one of the most convenient and simple ways of obtaining thin oxide films in non-equilibrium conditions with formation of metastable structural and chemical phases displaying required properties [Alphonse et al., 2010; Wang et al., 2009].

For the realization of the process of electrochemical titanium oxidizing, using a simple electric chain is enough (Fig. 5). The electrochemical cell represents the two-electrode system consisting of the titanium anode and the corrosion-resistant steel cathode connected to the direct current source.

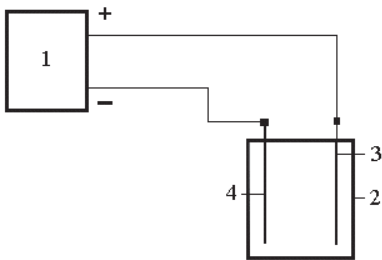


Fig. 5. The block diagram of a cell for titanium anodization process: 1 – power supply; 2 – electrochemical cell; 3 – anode; 4 – cathode.

Titania-based films obtained using electrochemical oxidation of metallic titanium possess an interesting microstructure. During anodic oxidation on the titanium surface the porous titania film is formed, consisting of a mass of nanotubes oriented perpendicularly to metal substrate whose diameter can be varied within several tens of nm depending on parameters of electrochemical process [Gong et al., 2001; Macak et al., 2005; Paulose et al., 2007]. The choice of suitable modes of anodic oxidation allows to obtain porous titania films with the required pore sizes and good homogeneity.

To determine the effect of solvent nature on the kinetics of anodic process, we have recorded the chronoamperometric curves for EG and DMSO-based electrolytes (Fig. 6).

In chronoamperograms the initial part of titanium anodizing process is reflected. Initial current density in EG-based electrolytes is twice as much compared to DMSO-based ones. It can be attributed to the different electrical conductivities of the given solutions. The specific electrical conductivity of EG-based electrolyte is $8,72 \cdot 10^{-3}$ S/m whereas that for DMSO-based solution is $3,97 \cdot 10^{-3}$ S/m.

In the DMSO-based solutions upon exposure to direct voltage the current decline occurs at a smaller speed as compared to EG-based electrolytes that testifies to the formation of an oxide layer with more advanced surface. In EG-based electrolytes a sharp current decline is observed, that testifies to the formation of titania layer in a shorter time.

Photoelectrochemical properties of the surface layers generated on titanium by anodic oxidation were investigated in background electrolyte 0.2M Na_2SO_4 . The photoresponse with negative sign testifies to the formation on the titanium surface of a non-stoichiometric oxide with lack of oxygen and electronic type of conductivity. For the purpose of increasing the photoresponse of titania films obtained using anode oxidation, we additionally performed thermal treatment directly after anodizing process.

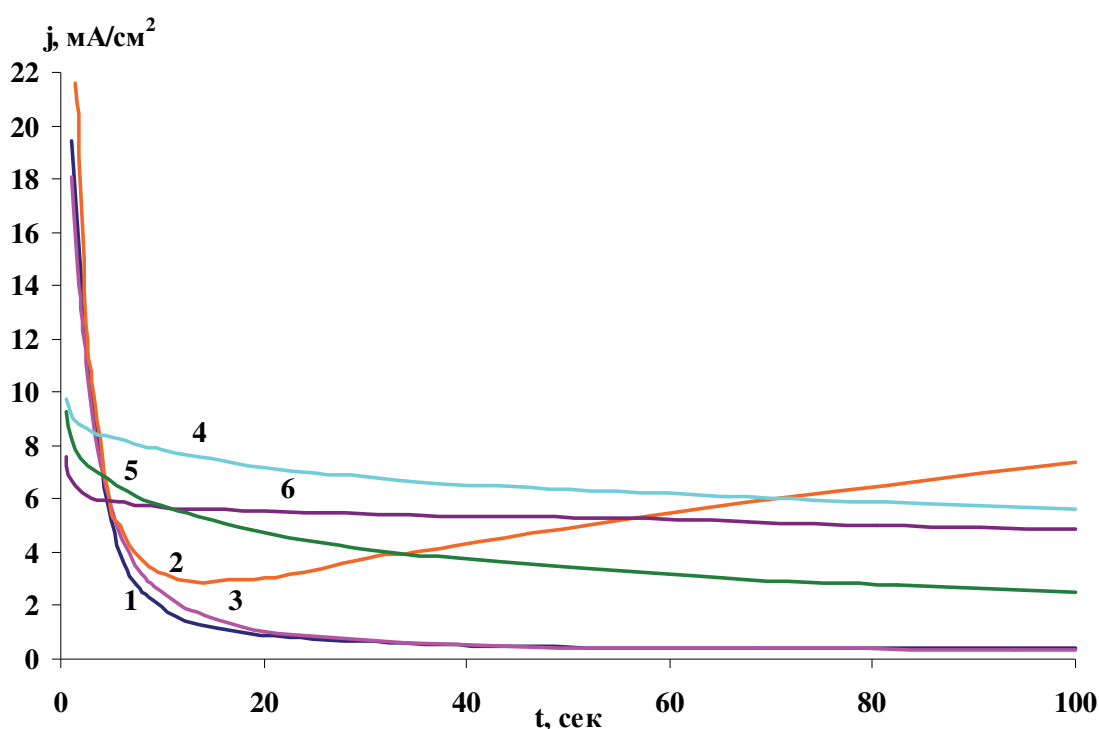


Fig. 6. Chronoamperometric curves of titanium electrode in electrolytes: 1 – EG + 2.5 g/l NH_4F ; 2 – EG + 2.5 g/l NH_4F + 0.15 g/l PcCo ; 3 – EG + 2.5 g/l NH_4F + 0.15 g/l $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$; 4 – DMSO + 0.5 g/l NH_4F + 5% H_2O ; 5 – DMSO + 0.5 g/l NH_4F + 5% H_2O + 0.15 g/l PcCo ; 6 – DMSO + 0.5 g/l NH_4F + 5% H_2O + 0.15 g/l $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$. $T = 293 \text{ K}$. Cell voltage is 20 V.

For increasing the photocatalytic properties of titania films we have chosen the higher macroheterocyclic compounds (porphyrins and phthalocyanines), and also their metal-containing complexes. Metal-containing porphyrin and phthalocyanines complexes possess unique optical, semiconductor and catalytic properties, therefore are of interest for researchers in the field of chemistry, biology, medicine, optics and materials technology.

It is seen from the Table 1 that the greatest photo-EMF magnitudes are exhibited by titania films obtained in DMSO solution containing 0.15 g/l of cobalt phthalocyanine, and that is apparently related to introduction of the latter into porous structure of the oxide layer.

Solution composition	V _{PEP} , mV for thermal treatment time, min		
	0	30	60
EG+2.5 g/l NH ₄ F	-1	-30	-32
EG +2.5 g/l NH ₄ F + 0.15 g/l CoSO ₄ ·7H ₂ O	-8	-60	-61
EG +2.5 g/l NH ₄ F + 0.15 g/l PcCo	-7	-58	-59
DMSO + 5 % H ₂ O + 0.5 g/l NH ₄ F	-10	-61	-62
DMSO + 5 % H ₂ O + 0.5 g/l NH ₄ F + 0,15 g/l CoSO ₄ ·7H ₂ O	-10	-61	-62
DMSO + 5 % H ₂ O + 0.5 g/l NH ₄ F + 0,15 g/l PcCo	-20	-68	-68

Table 2. The photoelectropolarization (V_{PEP}) magnitudes for a titanium electrode after anodization within 60 minutes in DMSO solutions with addition of Co-containing salts and thermal treatment at T = 523 K.

The photo-EMF magnitudes for titania films obtained within 1 hour of anodic oxidation in solutions with different concentrations of PcCo, are listed in Table 3. It is seen from the table that the photoelectropolarization magnitudes directly after anodization process range from 20 to 40 mV, the introduction of PcCo into solution leading to an increase in the photo-EMF magnitudes, and that is related to an introduction of PcCo into the structure of the oxide layer. After thermal treatment the photo-EMF magnitudes increase. The increase in the photo-EMF magnitudes can also be related to the increase in activity of PcCo as a result of thermal treatment.

Solution composition	V _{PEP} , mV for thermal treatment time, min		
	0	30	60
DMSO + 0.05 g/l NH ₄ F + 5% H ₂ O	-24	-40	-60
DMSO + 0.05 g/l NH ₄ F + 0.05 g/l PcCo + 5% H ₂ O	-40	-63	-64
DMSO + 0.05 g/l NH ₄ F + 0.15 g/l PcCo + 5% H ₂ O	-41	-62	-68

Table 3. The photoelectropolarization (V_{PEP}) magnitudes for a titanium electrode after anodization within 60 minutes in solutions with different concentrations of PcCo and thermal treatment at T = 523 K.

We have also investigated the effect of additives of metal-containing porphyrin and phthalocyanines complexes of various nature. In Table 4 we list the photo-EMF magnitudes for titania films obtained from solutions with addition of macroheterocyclic compounds of various composition – cobalt phthalocyanine (PcCo), cobalt porphyrin (PhCo) and deuteroporphyrin (DtPh). It is notable that the greatest photoactivity is exhibited by films obtained from solutions with addition of PcCo.

Solution composition	V _{PEP} , mV for thermal treatment time, min		
	0	30	60
DMSO + 0.5 g/l NH ₄ F + 5% H ₂ O + 0.05 g/l PcCo	-40	-63	-64
DMSO + 0.5 g/l NH ₄ F + 5% H ₂ O + 0.05 g/l PhCo	-1	-61	-61
DMSO + 0.5 g/l NH ₄ F + 5% H ₂ O + 0.05 g/l DtPh	-2	-57	-60

Table 4. The photoelectropolarization (V_{PEP}) magnitudes for a titanium electrode after anodization within 60 minutes in solutions with different additives before and after thermal treatment at T = 523 K.

Introduction of the cobalt phthalocyanine additive into DMSO-based anodizing electrolyte leads to a decrease in the rate of anodic titanium oxidation. Titania layers formed during the process exhibit increased photo-EMF magnitudes. Oxide structures obtained using the method of anodic titanium oxidation in DMSO-based solutions with the cobalt phthalocyanine additive can be usefully applied in photoelectrochemical processes.

10. Sensitization of metal-oxide electrode surfaces using dyes

As the own absorption region of titanium dioxide ($\lambda < 380\text{ nm}$, $h\nu \geq 3.2\text{ eV}$) is affected by less than three percent of solar irradiation, it is sensitized to visible region. One of the ways to increase the efficiency of excitation process for wide-zone semiconductors is chemical or physical sorption of dyes. Expansion of region of operating light is possible at the expense of dye excitation by long-wave light and then by the charge transfer to the semiconductor, Fig. 7.

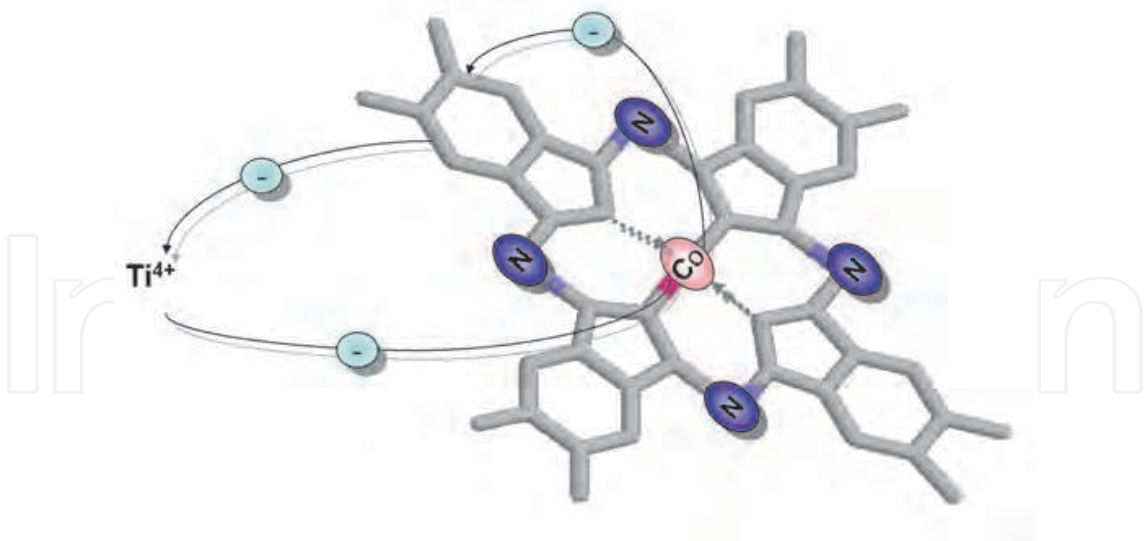


Fig. 7. An example of formation of a thin-film PcCo complex to an efficient electron acceptor – semiconductor oxide particle.

If distributions of the excited dye levels are intersected with zones of resolved energies of the semiconductor – electrode, and there is no non-excited one, then electronic transition between the electrode and the solution, i.e. the course of an electrochemical reaction, is possible only upon irradiation.

In our investigations [Vinogradov et al., 2008] modifying sol-gel synthesis by introduction of water-soluble PcCo as an organic sensitizer in the stage of formation of titania sol particles have also allowed to increase photoactivity of formed hybrid nanomaterials. In this work, using the given photopolarization measurements it has been shown that photocatalytic activity for an organic-inorganic composite titania-PcCo obtained by sol-gel technology depends on conditions of material synthesis and can be considerably higher than for a pure titania, see Table 5.

Substance	T, °C thermal fixation	Electrode	Photo-emf of electrode without deposited composite	Photo-emf, mV	Gain in photo-emf
TiO ₂ , pH 4	250	Ni	0.44	1.5	3.4
TiO ₂ , pH 11	250	Ni	0.34	6.8	20
PcCo + TiO ₂ , pH 4	250	Ni	0.44	7	15.9
PcCo + TiO ₂ , pH 5	250	Cu	6	9	1.5
PcCo + i-I	180	Ni	0.44	0.7	1.6
PcCo + TiO ₂ , pH 11	180	Ni	0.34	0.5	1.47
TiO ₂ , pH 11	180	Ni	0.34	0.74	2.18

Table 5. Photo-emf response of the films under UV irradiation.

11. Doping of organized semiconductor by introducing metal nanoparticle layer

Putting a metal layer on a semiconductor for the purpose of increasing its photoactivity is well-known and successfully used technique. Metal is put either in the form of a continuous thin film to let the radiation pass through the metal – semiconductor interface, or in the form of nanoclusters or large-pore films on the semiconductor surface, assuming its direct contact to electrolyte.

Precipitation of precious metals onto the semiconductor surface, as a rule, substantially changes the properties of the surface and thereby strongly affects the photocatalytic process with its participation. Metal can change composition of products or rate of photocatalytic reaction. An increase in the reaction rate was for the first time observed in the case of Pt/TiO₂ during reactions of water decomposition into oxygen and hydrogen. In [Gnaser et al., 2004] it is said that Pt, Pd, Rh increase the rate of hydrogen production by 20-100 times whereas putting iron suppresses hydrogen production.

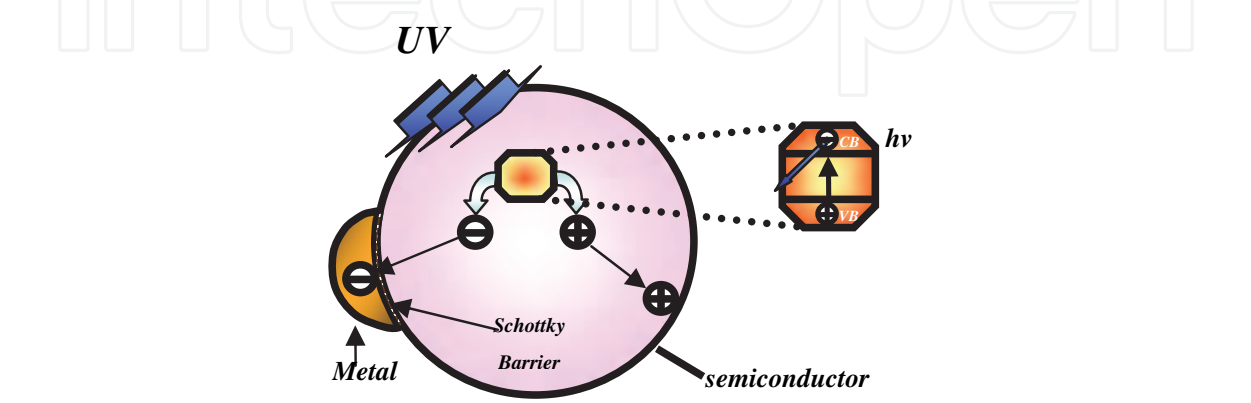


Fig. 8. Metal-modified semiconductor photocatalyst particle.

After excitation, an electron migrates towards metal by which it is grabbed, so electron-hole recombination is suppressed. Migration of electrons towards metal particles is confirmed by investigations showing a decrease in the semiconductor photoconductivity upon putting Pt on TiO_2 (as compared to pure TiO_2). But holes appear to be free enough to diffuse towards semiconductor surface, and then to enter reactions, for example, oxidations of organics. In practice the Pt/ TiO_2 system is especially widely used. Platinum introduction onto the TiO_2 surface appears to be especially efficient for photocatalytic reactions in which gas is produced, in particular, hydrogen.

Along with doping by precious metals a special attention is recently paid to modifying the photocatalysts by the f-element impurities [Mazurkiewicz et al., 2005]. As the investigations reveal, all f-elements can be divided into two groups: Nd, Pm, Gd, Ho, Er, Lu which exhibit valence (III), and Ce, Pr, Sm, Eu, Tb, Dy, Tm, Yb, demonstrating variable valence (II), (III), (IV). According to the obtained data, the most efficient impurities are Pr, Sm, Eu, Dy, and Tm, i.e. f-elements with variable valence.

Apparently, upon absorption of UV-light quanta there is an increase in concentration of paramagnetic Ti^{3+} ions at the expense of free electrons: $\text{Ln}^{3+} + h\nu = \text{Ln}^{4+} + \bar{e}$. Besides, among the entire row of f-elements it is necessary to note Tm^{3+} to be the most efficient TiO_2 activator. According to the principle of lanthanide contraction, Tm^{3+} has the least ionic radius. Thus, the Tm^{3+} ions regarding the spatial-energetic relation possess higher probability to penetrate into the TiO_2 layer and to act as electron donors or the impurity adsorption centers, i.e. both collective and individual factors of affecting the state of the photocatalyst surface take place.

Modifying titania by certain impurities and preliminary thermal treatment in a reductive environment allows, within certain frameworks, to control its photocatalytic activity.

One of the goals of our investigations started in 2010 was modifying the surface of the TiO_2 film by various metals in colloidal state, such as Cu, Ag, Fig.9, which would allow, on the one hand, to achieve photochromic effect without the traditional usage of platinum and palladium, and, on the other, to increase the photoactivity of the generated composites.

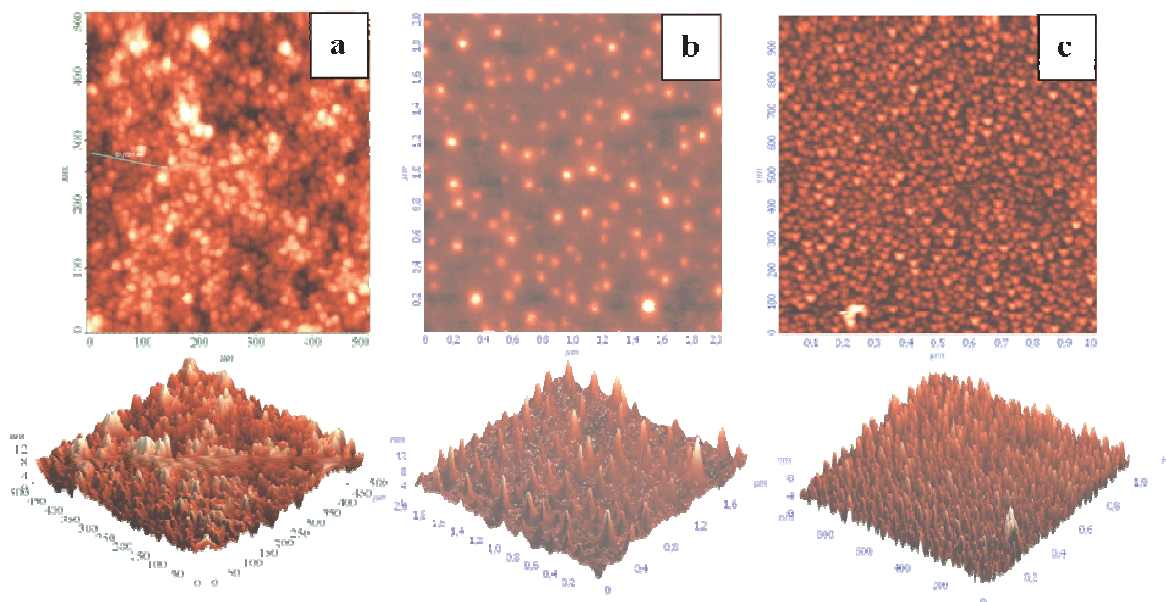


Fig. 9. The AFM images: a) the surface of the TiO_2 film; b) the surface of the Cu- TiO_2 film; c) the surface of the Ag- TiO_2 film.

Thus, the necessary factor was obtaining the nanoparticles with sizes in the range of 10 nm, leading to the generation of heterostructures of the metal nanoparticles plasmon resonance in the system. As a result of processing the AFM images, it was revealed that the copper nanoparticles generated in the conditions of the Cu²⁺ reduction using sodium tetrahydroborate, Fig. 9b, possess spherical form and narrow particle size distribution of about 8 nm. According to Fig.9(c), the generated Ag nanoparticles represent triangular nanoprisms with the average size of about 5 nm distributed in regular intervals on the TiO₂ surface.

Sample	Photo-emf (non-calcined), mV	Conductivity type
TiO ₂ +Ag	46	p-
TiO ₂ +Cu	32	p-
TiO ₂ non-modified	15	n-

Table 6. The photoactivity characteristics of composite materials obtained using metal nanoparticles.

The data implying high photoactivity of the Ag/TiO₂ composite are confirmed by the greatest photoresponse value of 46 mV, Table 6. After UV irradiation the excited electrons move towards the TiO₂ conductivity zone, and holes move towards the valence zone through interface. Thus, the separation of the photogenerated electron-hole pairs in a composite film is more efficient than in pure, non-modified one. Hence, the recombination of the photogenerated charge carriers also proceeds more efficiently, and that is proved by an increase in the photoresponse value for the composites used. The use of copper and silver nanoparticles also promotes the increase in photocatalytic activity of a film, Table 6, owing to larger water adsorption on the surface of a composite due to the nanoparticle surface effect [Agafonov et al., 2009], which is promoted by a high concentration of the photogenerated holes whose presence is confirmed by composite conductivity type, Tab.6.

12. Using template synthesis for obtaining materials with high photoactivity

The analysis of literature data has shown that for studying photoactivity of titania-based materials the spectroscopic investigations aimed at studying photochemical reactions on the surfaces of materials are the most used. However, such an approach allows to only partially describe the processes of charge transport and effects of internal structure on photoactivity of a material as a whole. As has been shown, the greatest complications arise in the presence of considerable structural impurities in the lattice structure, and also in the presence of a bulky structured surface. The presence of highly electronegative elements in crystal structure, which act as electron donors, considerably complicates the process of charge transport, and such materials will be characterized, as a rule, by either hole or ionic type of conductivity. Thus it is necessary to perform a complex estimation of photoactive properties of synthesized materials which would allow to consider simultaneously the role of structure and nature of a material. Using template synthesis, on the one hand, allows to form various highly arranged structure of materials in mesoregion and, on the other, in the course of removing templates by thermal treatment, leads to an increase or a decrease in photoactivity (depending on type of structure of generated crystallites) because of remaining presence of impurity ions, such as C, N, O etc. Thus, the most fair is the use of a combination of two

methods – method of photoelectric polarization of films and analysis of kinetic curves of a model dye photodestruction which provide the accounting for both the effect of the structural factor and own semiconductor properties on the total photocatalytic properties.

The most interesting study is supposed to be that of functional properties of the preparations obtained using templates which differ by their chemical nature: dodecylamine (DDA), polyethylenimine (PEI), polyethylene glycol monooleate (PEGMO), polyethyloxazoline (PEOA). The structure of hybrids obtained with their participation is shown in Fig. 10.

It is seen from the presented figures that using various modifying additives leads to various organizations of the surface. In Fig. 10a the structure of the TiO_2 film formed by hierarchical pores of the roundish shape ($\varnothing \approx 105 \text{ nm}$) with uniform morphology is shown. The films obtained using dodecylamine, are characterized by pores with the narrowest size distribution ($\varnothing \approx 30 \text{ nm}$). The films generated with participation of PEGMO, are covered with oval pores with the maximum length of 150 nm, and the length to width ratio of about 5. It is obvious that the pore size is related to the degree of hydrophobicity of a template. The materials including hydrophilic PEI and PEGMO reveal larger pores than with hydrophobic DDA. At the same time, it has been established that for the films generated using tertiary amines, fig. 10d, the formation of planar structure is observed, with “islet” inclusions which are distinguished by a chaotic spatial organization with non-uniform formations. It points to the fact that the coordination activity of the stabilizer is low. Thus, for the films obtained as a result of isopropylate hydrolysis in the presence of polyethyloxazoline we can observe separate formation of large agglomerates of hydrated titania and planar structures of polymer – polyethyloxazoline (fig. 10d).

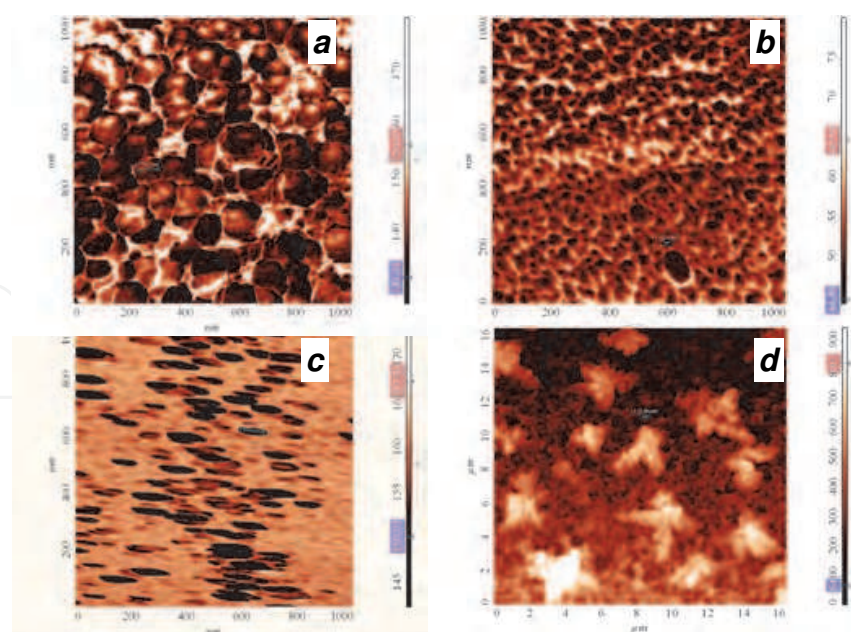


Fig. 10. The surfaces of hybrid films modified by a) polyethylenimine; b) dodecylamine; c) polyethylene glycol monooleate; d) polyethyloxazoline.

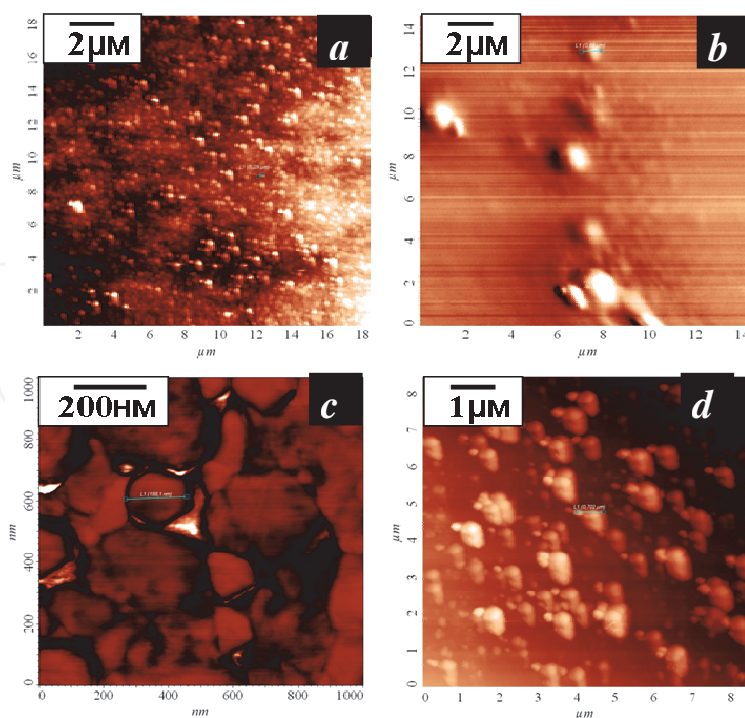


Fig. 11. The surfaces of calcined (at 300°C) films modified by: a) polyethylenimine; b) dodecylamine; c) polyethylene glycol monooleate; d) polyethyloxazoline.

Among the obtained materials, the greatest gain in photo-EMF is exhibited by the calcined films generated in the presence of polyethyloxazoline and polyethylene glycol monooleate – templates with the least coordination activity leading to the formation of defective crystallites and n-type conductivity.

The primary and secondary amines which are characterized by high coordination activity, during synthesis promote formation of stable inorganic frameworks in which nitrogen is chemically bonded to Ti^{4+} . After calcination in such materials the accepting impurity of nitrogen remains, which forms additional energy levels. It is necessary to note that using polyethylenimine as a template allowed to generate films with high photoactivity, both in non- calcined (2.8 mV), and in calcined form (20 mV), due to the presence of a larger number of developed electron accepting impurity centers that promote narrowing of the bandgap, and, as a consequence, a "readier" formation of electron-hole pair. Comparison of photoactivity of thin TiO_2 -based coatings obtained using various methods allows to make a conclusion about the prospects of using modifying additives for the purpose of increasing the quantum yield, as in this case photogenerated electron-hole pairs in the TiO_2 nanoparticles possessing short-range order are separated more efficiently than in pure TiO_2 . Thus, the excess of accepting impurity in the structure of crystal lattice can delay the recombination of photogenerated electrons and holes and thereby promotes increase in the TiO_2 photocatalytic activity.

The film photoactivity evaluation was performed using photo-emf data upon the brief irradiation by a 250 W UV lamp; a platinum screen served as the second electrode. The data obtained are listed in Table 7.

TiO_2 is known to be indirect bandgap semiconductor characterized by electronic conductivity type. This charge transport mechanism is due to the formation of O^{2-} vacancies in the crystal lattice structure, the two neighbor Ti^{4+} ions acquiring the 3^+ charge. It leads to

the appearance of a weakly connected electron on their outer electron shell bringing about the conductivity type. The presence of highly electronegative elements acting as electron donors in crystalline structure significantly impedes the charge transport process, and such materials will as a rule be characterized by hole or ionic conductivity type.

Modified TiO ₂ sample	Surface pore diameter, nm	Average crystallite size	V, cm ³ /g	D _{pore} , Å	Conduc-tivity type	Photo-emf, mV
Polyethyloxazoline	112	2	0.035	117	N-	45
Polyethylenimine	105.2	2.5	0.584	282	P-	20
Dodecylamine	49.3	1.7	0.174	58	P-	1.5
PEG monooleate	17.8–92.4(L)	2.1	0.265	110	N-	22.5

Table 7. The resulting table of physico-chemical and structural properties.

The assumption of low coordination activity of polyethyloxazoline is also confirmed by the data from Table 7. For such a film, the greatest photo-EMF of 45 mV caused by the formation of the least defective crystals and n-type conductivity is found. For comparison, the characteristic of TiO₂ film modified by PEG monooleate is given, indicating the low coordination activity in complexation reactions. The data obtained show that the both films possess high photoactivity and n-type conductivity.

The primary and secondary amines characterized by high coordination activity promote the formation of stable inorganic frameworks during the synthesis process. In these frameworks nitrogen is chemically bonded to Ti⁴⁺. After calcination these materials retain the acceptor impurity of nitrogen that forms additional energy levels. At the same time, using the polymer molecule, i.e. polyethylenimine as a template promotes the formation of films with highly developed surface and photoactivity due to the presence of a large number of developed electron acceptor groups. In the diethylamine–octylamine–dodecylamine series the photoactivity decreases drastically as the basicity of an amine decreases.

13. Conclusion

Thus, using method of photoelectric polarization for estimating the functional properties of the materials used upon manufacturing photocatalysts and solar cells acting on the basis of the modified solid-state semiconductors is the most universal and readily available technique. In the given chapter we have shown the basic ways promoting the increase in photoactivity of titania-based materials obtained by anodic oxidation and sol-gel method. Among those are using ultrasonic treatment, modifying by phthalocyanines and metal nanoparticles, formation of highly developed surface, doping with metals and non-metals. The fundamental aspects of the photo-EMF emergence in nanomaterials upon electrode irradiation in a solution in combination with the resulted data which have been considered in this chapter allow to use competently the described method and apply it for estimating the photoactivity of materials.

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