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# Photoelectrochemical Photocurrent Switching Effect in Nanostructured Anodized Titanium Dioxide and Enhancement of its Photocatalytic Activity by Layer-by-layer Polyelectrolyte Assembly

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**Abstract:** This article reports effect of photoelectrochemical photocurrent switching on anodized titanium dioxide which was observed for the first time for this material. When negatively polarized,  $\text{TiO}_2$  photoelectrode gave anodic photocurrent under 365 nm irradiation and cathodic one under 405 nm irradiation. We suppose, this phenomenon can be explained by electron pathways provided by  $\text{Ti}^{3+}$  states occurring in anodized  $\text{TiO}_2$  during annealing. We also demonstrate here effect of anodic photocurrent increase after photoelectrode surface was modified by  $(\text{PSS}/\text{PEI})_3$  Layer-by-layer assembly. Photoanodic performance is three times higher for  $\text{TiO}_2/(\text{PSS}/\text{PEI})_3$  than for bare  $\text{TiO}_2$ .

**Keywords:** photochemistry,  $\text{TiO}_2$ , photocurrent switching, layer-by-layer assembly

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## 1. INTRODUCTION

Titanium dioxide is one of the most studied materials. However, it still attracts great attention of researchers [1, 2]. Due to its low toxicity, high stability, low cost, and stable photoactivity,  $\text{TiO}_2$  is considered as a promising photocatalytic material, which is already widely used in the development of solar cells [3], and photocatalysts for water [4] and air [5] purification.

There is high interest in titanium dioxide as photocatalyst. It exists in several

crystalline modifications (rutile, anatase, brookite) and various forms (nanoparticles, nanotubes [6], nanofibers [7] and nanosheets [8]) and photocatalytic characteristics are highly dependent on crystallinity [9], phase composition, and method of the material obtaining [10]. The photoelectrochemical behavior can also be changed by doping [11] and surface modification [12, 13]. Establish a relationship between photocatalyst morphology, elemental, and phase composition is a task of fundamental importance.

In this paper, we consider highly ordered arrays of titanium dioxide nanotubes obtained by anodic oxidation of titanium plate [14]. When  $\text{Ti}/\text{TiO}_2$  is irradiated, an electron-hole pair formation occurs. Ordered tubular

nanostructures are characterized by large active areas and low recombination rates [5]. Therefore, anodized TiO<sub>2</sub> nanotubular arrays are more photocatalytic efficient compared to disordered forms of titanium dioxide [14].

It was recently demonstrated that significant pH-gradient could be obtained by local irradiation of the surface of the TiO<sub>2</sub> nanotubes. Local radiation of the planar photoelectrode surface creates a “conductive point” serving as a photoanode. The bending of the semiconductor zones and the Schottky junction at the Ti-TiO<sub>2</sub> interface cause spatial separation of charges: photoexcited holes ( $h^+$ ) reach the interface between titanium tubes and an aqueous solution. Holes, which are active oxidizing agents, cause the photolysis of water and hence trigger the flow of protons from the illuminated region. Thus, titanium dioxide nanotubes can be used to trigger local proton fluxes [15]. At the same time, electrons are transferred to the Ti-TiO<sub>2</sub> interface and then through the metal substrate to the external circuit. As a result, the anodic photocurrent is observed.

Thus, the use of photoconductive substrates makes it possible to create a flexible and customizable electrode system for generating the desired pH gradients. Changing the polarization allows switching the activity of the photoconductive electrode from the photocathodic at negative applied voltage to the photoanodic at a positive one. As a result, hydroxide ions or protons may be produced respectively locally inside irradiated spots [16].

The effect of the photocurrent switching [17] when switching illumination from ultraviolet to blue was observed in

nanostructured anodized titanium dioxide at a fixed potential. This effect has been previously described for a limited number of materials, such as bismuth orthovanadate, lead molybdate, V-VI-VII semiconductors, and, for example, photoelectrodes made of nanocrystalline TiO<sub>2</sub> modified by cyanoferrate [14, 18] and ruthenium [19] complexes, thiamine, folic [20] and carminic [21] acids. For unmodified nanostructured anodized, this effect is described for the first time in this work.

Layer-by-layer (LbL) polyelectrolyte assembly is a convenient and straightforward way to modify and functionalize the surface. This approach is widespread in the development of functional coatings, such as anticorrosive and antimicrobial [22, 23]. Recently, it was also shown that LbL assemblies on the surface of photoelectrodes could affect their photocatalytic properties [11]. In particular, it was demonstrated that photoelectrodes fabricated from a suspension of TiO<sub>2</sub> particles coated with sodium polystyrene sulfonate (PSS) show a higher efficiency of photocatalytic decomposition of organic dyes compared to unmodified particles [24].

## 2. MATERIALS AND METHODS

Titanium plates with a thickness of 1 mm and a purity of 99.6% were used. The plates were etched in a mixture of concentrated hydrofluoric and nitric acids in a ratio of 1:2. Highly ordered photoactive arrays of titanium dioxide nanotubes were obtained by two-stage anodizing of titanium plates with a platinum counter electrode of the same area. Ethylene glycol containing 0.75% NH<sub>4</sub>F and 2% distilled water was used as an electrolyte for anodizing. At the first stage, the titanium anode was polarized in a linear

sweep mode with a voltage from 0 to 40 V and a potential sweep speed of 0.2 V/s. At the second stage, the same titanium plate was polarized by applying a constant voltage of 40 V for an hour. The obtained nanotubes are then treated with ultrasound in ethanol for 0.5-1 min and annealed at 450°C for 3 hours.

The phase composition of the samples was studied by X-ray diffraction (XRD) using  $\text{CuK}\alpha$  irradiation ( $\lambda = 1.5405 \text{ \AA}$ ). Diffractograms were obtained in the range of  $2\theta$  from 2 to 60, with a scan rate of 5°/min.

The morphology of  $\text{TiO}_2$  coatings was investigated by Scanning Electron Microscopy (SEM) using a Hitachi S-4800 microscope (Hitachi High-Technologies Inc., Japan). Previously, a carbon layer was sprayed onto the samples to improve contrast.

Chronoamperometry measurements were performed in a standard three-electrode cell filled with 0.05 M NaCl with a photoactive plate of anodized nanostructured  $\text{TiO}_2$  as a working electrode, a platinum counter electrode, and Ag/AgCl reference electrode using PalmSens4 potentiostat (Netherlands). Ultraviolet (365 nm) and blue (405 nm) 5 mV/cm<sup>2</sup> light-emitting diodes were used as radiation sources. The working surface of the electrode was 0.2 cm<sup>2</sup>. The dark current was first recorded at the applied potential, then the light source was turned on, and the photocurrent was recorded for 10 minutes. The data were presented as the dependence of the current density on time.

Polyelectrolyte layers were deposited using the classical LbL approach. Solutions of polycation - polyethyleneimine (PEI) and polyanion - polystyrene sulfonate (PSS) were

dissolved in 0.5 M NaCl solution to obtain 2 mg/ml polymer solutions. Branched PEI (Mw 70000), 30% aqueous solution, and PSS (Mw 500000), both Sigma Aldrich, were used.

Each polyelectrolyte layer was deposited by immersion of titanium nanotubes substrate in a solution of the corresponding polyelectrolyte. After each immersion, the sample was rinsed with distilled water. As a result, the LbL assembly of (PSS/PEI)<sub>3</sub> architecture was deposited on top of the Ti/ $\text{TiO}_2$  substrate.

The photocatalytic activity of nanostructured anodized titanium dioxide was also studied using a Scanning Vibrating Electrode Technique (SVET) using a system from Applicable Electronics (USA) under the control of ASET software (Sciencewares, USA). The SVET method allows one to visualize the distribution of anodic and cathodic activity regions by measuring the electric field in a solution near the surface of the sample. The potential,  $\Delta V$  between two points at a distance  $\Delta r$  from each other was measured for these purposes. It is realized using a vibrating electrode scanning the surface in SVET.

Pt-Ir microprobe (Microprobe Inc., USA) coated with an insulating polymer and with a spherical platinum black tip with a diameter of 30  $\mu\text{m}$  was used as a vibration probe. A piezoelectric generator set the vibration, the probe oscillation frequency was 136 Hz, and the amplitude was 30  $\mu\text{m}$ . The probe was located at the height of 150  $\mu\text{m}$  above the sample. The measured potential  $\Delta V$  was then recalculated to the local current density following a preliminary calibration.

### 3. RESULTS AND DISCUSSION

The XRD pattern of anodized titanium dioxide contains peaks at 25, 38, 48, 54, and 55° 2θ, which indicates the formation of an anatase TiO<sub>2</sub> phase (Fig. 1a). Electron microscopy demonstrates the formation of highly ordered and vertically arranged nanotubes with a pore diameter of approximately 60-80 nm (Fig. 1b).

Highly ordered TiO<sub>2</sub> nanotubes are characterized by short charge transfer distance and small losses during the recombination of an excited electron-hole pair [14]. Therefore, titanium nanotubes obtained by titanium anodization demonstrate greater efficiency of photoelectrochemical processes in comparison with nonoriented and disordered forms of TiO<sub>2</sub>.

The anatase band gap is 3.2 eV. Thus, anatase optical absorption is limited by the ultraviolet region, and this phase of TiO<sub>2</sub> exhibits photocatalytic activity only when irradiated with ultraviolet light (λ < 390 nm). Ultraviolet radiation (λ = 365 nm) excites an electron from the valence band (VB) directly to the conduction band (CB) of TiO<sub>2</sub>. Under conditions of thermodynamic equilibrium with the electrolyte solution, semiconductor zones bending occurs. This phenomenon prevents the injection of electrons into the solution and forces the electron transfer to

conducting titanium substrate and then to the external circuit (Fig. 2a).

Weak current flows during anodic polarization (+0.3 V) of TiO<sub>2</sub> photoelectrode. When ultraviolet (365 nm) irradiation is switched on, a sharp increase in current and reaching a stable value is observed. A fast and steady increase/decrease of the photocurrent value upon switching on/off irradiation indicates an effective separation of charges and their low recombination rate (Fig. 2c).

During the anatase phase forming annealing of titanium nanotubes in a non-oxidizing atmosphere, partial titanium reduction occurs. As a result, intermediate Ti<sup>3+</sup> energy levels are formed in the bandgap of titanium dioxide. These levels create additional electron transfer pathways [25] and make titanium nanotubes photoactive in the visible part of the spectrum, in particular, when irradiated with blue light (λ = 405 nm) (Fig. 2b). Compared to UV light, the blue one (λ = 405 nm) is characterized by lower energy and is not able to excite electrons directly to the conduction band, because the bandgap is higher than the energy of blue irradiation.

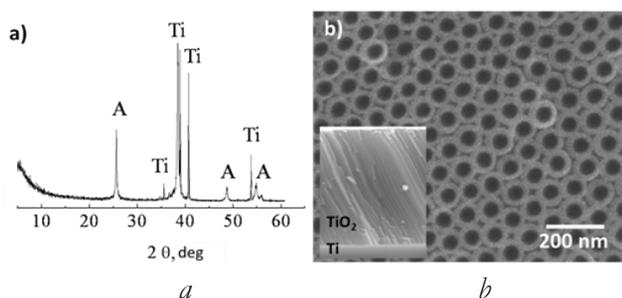


Fig. 1. a) XRD pattern of titanium dioxide obtained by double anodic oxidation of titanium, b) SEM micrographs of the TiO<sub>2</sub> nanotubes surface obtained by double anodic oxidation of titanium.

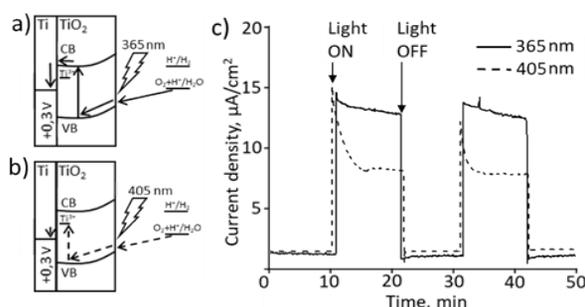


Fig. 2. Schemes of energy levels (VB - valence band, CB - conduction band) and electronic transitions in anodized nanostructured TiO<sub>2</sub> at a potential of +0.3 V and when irradiated a) with ultraviolet light (λ = 365 nm), b) with visible blue light (λ = 405 nm), c) chronoamperometric measurements at a potential of +0.3 V and chopped irradiation.

However, an electron excited by blue light can be trapped by  $Ti^{3+}$  levels and transferred to a conducting titanium substrate (Fig. 2b). When exposed to visible light, the initial current spike is followed by an exponential photocurrent decay, suggesting a fast recombination process (Fig. 2c).

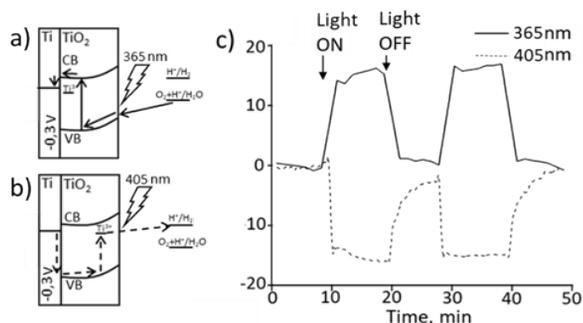
The effect of photocurrent switching depending on irradiation wavelength is observed at negative polarization (-0.3 V) in nanostructured anodized titanium nanotubes. Depending on the wavelength of irradiation, an anodic or cathodic photocurrent was registered in an external circuit. In the case of negative polarization and ultraviolet radiation, the excited electron passes into the conduction band and hence to the conductive substrate and the external circuit (Fig. 3a). As a result, a positive photocurrent is recorded (Fig. 3c).

The energy levels of  $Ti^{3+}$  located in the bandgap of  $TiO_2$  capture electrons excited by visible light with an energy less than the bandgap. With negative polarization, electron transfer from this level to the oxidizing agent in solution (water) is more advantageous. In

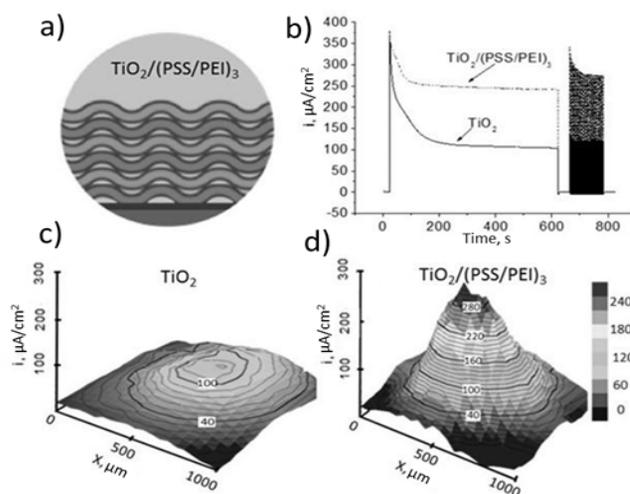
this case, a negative photocurrent is observed (Fig. 3c).

Thus, with the same polarization, the photoactivity of anodized nanostructured titanium dioxide can be changed from cathodic to anodic and vice versa using radiation with different wavelengths, for example, ultraviolet and visible blue.

The possibility to control the photocatalytic properties of nanostructured anodized titanium dioxide by modifying its surface with polyelectrolyte assemblies was also investigated. The photoanodic activity of titanium nanotubes upon irradiation with a focused light spot ( $\sim 500 \mu m$ ) of ultraviolet radiation was studied. Then, a polyelectrolyte multilayer of  $(PSS/PEI)_3$  (Fig. 4a) was deposited on top of  $TiO_2$ , and measurements were repeated under the same conditions.



**Fig. 3.** Schemes of energy levels (VB - valence band, CB - conduction band) and electronic transitions in anodized nanostructured  $TiO_2$  at a potential of -0.3 V and when irradiated a) with ultraviolet radiation ( $\lambda = 365 \text{ nm}$ ), b) visible blue light ( $\lambda = 405 \text{ nm}$ ), c) chronoamperometric measurements at a potential of -0.3 V and chopped irradiation.



**Fig. 4.** a) Schematic image of titanium dioxide surface coated with a polyelectrolyte multilayer of  $(PSS/PEI)_3$ , b) chronoamperometric measurements of unmodified nanostructured anodized titanium dioxide and the same sample coated with  $(PSS/PEI)_3$  polyelectrolyte multilayer under and chopped irradiation, c) map of photoelectrochemical activity obtained by SVET method in solution over a  $TiO_2$  sample irradiated with a focused UV ( $365 \text{ nm}$ ,  $5 \text{ mW/cm}^2$ ), d) map of photoelectrochemical activity obtained by SVET method in solution over a  $TiO_2/(PSS/PEI)_3$  sample irradiated with a focused UV ( $365 \text{ nm}$ ,  $5 \text{ mW/cm}^2$ ).

An anodized titanium dioxide photoelectrode modified by polyelectrolytes generates approximately 2.5 times higher anodic photocurrent under ultraviolet irradiation than unmodified one (Fig. 4*b*).

The anodic and cathodic activity was mapped in solution over the surface of locally irradiated TiO<sub>2</sub> samples using the SVET technique. It was found that a region of anodic activity is localized inside irradiated spot on the surface of anodized nanostructured TiO<sub>2</sub>. The emerging electric field creates an ion flux of the order of 100 μA/cm<sup>2</sup> (Fig. 4*c*). For TiO<sub>2</sub>/(PSS/PEI)<sub>3</sub>, an increase in photoanode activity by approximately three times is observed, whereas localization is approximately the same (Fig. 4*d*).

#### 4. CONCLUSION

In this paper, we demonstrated the effect of photoelectrochemical photocurrent switching in nanostructured anodized titanium dioxide. Highly ordered arrays of titanium nanotubes were obtained by double anodizing of titanium plates. The morphology and phase composition of the Ti/TiO<sub>2</sub> composites were characterized, and their photocatalytic activity was studied. When photoelectrode negatively polarized, photocurrent direction changes depending on the wavelength excitation light: under UV irradiation ( $\lambda = 365$  nm), the photocurrent is positive, and under visible blue light ( $\lambda = 405$  nm) it is negative. Thus, it was shown that unmodified titanium dioxide shows the effect of photoelectrochemical photocurrent switching. The possibility of increasing the photoanodic activity of anodized TiO<sub>2</sub> by depositing polyelectrolyte assemblies on top of was also demonstrated.

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