Nature of paramagnetic defects in black titanium dioxide nanotubes

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HIGHLIGHTS

- Electrochemically obtained thin films of black and white carbon-containing TiNTs.
- EPR as a method for the reliable detection of C-radicals in titania nanotubes.
- According to EPR, carbon inclusions in titania are of aromatic structure.

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ABSTRACT

Electron paramagnetic resonance (EPR) spectroscopy was used to study the nature of defects in black titanium dioxide nanotubes (TiNTs) prepared by electrochemical oxidation of titanium in ethylene glycol. The TiNTs that have intensive black color were formed under thermal treatment of amorphous TiNTs in hydrogen at 500 °C. The work aimed to reveal the role of various defects in the black color of TiNTs. Amorphous carbon has been found to contribute mainly to the deep black color of anatase-type TiNTs. Considerable growth in •C-radicals concentration was detected by the EPR method in amorphous TiNTs under their heat-treatment in hydrogen. The radicals are resulted from the reduction of carbon-containing products of electrochemical and thermal decomposition of ethylene glycol. The dependence of the •C-radical signal position in EPR spectra on the axis of the applied magnetic field testifies for a predominant orientation of graphite-like networks along the direction of TiNTs growth. The Gaussian shape and broadness of the EPR lines are caused by the superposition of several signals from different carbon states. The conditions of synthesis that might result in the occurrence of Ti³⁺ state and oxygen vacancies in titanium oxide were analyzed. The absence of Ti³⁺ signals in the EPR spectra of TiNTs reduced in hydrogen can be explained by the high concentration of Ti³⁺ centers as well as by the formation of [Ti³⁺-VO-Ti³⁺] or [VO-Ti-VO]ⁿ⁻ complexes, which are inactive in EPR. The indicated defects might also contribute to titanium dioxide color.

1. Introduction

Black titanium dioxide has attracted considerable scientific interest since it differs in its functional properties from ordinary white TiO₂, which has no noticeable absorption in the visible-light region [1]. It has been shown that nanocrystalline TiO₂ powder Degussa P-25, reduced to a black state, is superior in photocatalytic and luminescent properties to the original white nanopowder [2,3]. This discovery intensified the search for new methods of obtaining black TiO₂ and studying its properties, taking into account various fields of application. It was

demonstrated that this material is promising as a photocatalyst for the generation of hydrogen from water or water-methanol solutions, material for supercapacitor electrodes, photoelectrochemical sensors, etc. [1,4,5].

Titanium dioxide usually changes its color from white to black under high-temperature treatment in a reducing atmosphere, e.g., in vacuum, argon, Ar/H₂ mixture, or pure H₂ [6–12]. Depending on the degree of reduction, it takes on a different color - green, yellow, brown, blue, grey, or black. However, it should be noted that achieving a deep black color in the case of TiO₂ with anatase structure is not an easy task. Under the

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same reduction conditions, when rutile becomes black, anatase becomes only grey [1,13]. Changes in the color and properties of TiO_2 have been associated with structural defects [6–11,13]. The color variation was explained by a different combination of defects: Ti^{3+} and oxygen vacancies [3,11–13]. The properties of black titanium dioxide are also influenced by surface Ti-OH [14,15] or Ti-H groups [16] and combinations of different types of defects [17–19]. The studies of the activity and properties of black TiO_2 were performed mainly on powder samples that did not contain uncontrolled impurities. However, the structural peculiarities and properties of black TiO_2 nanotubes (TNT) have been studied to a lesser extent compared to powders. Various methods have been proposed for obtaining black TiO_2 nanotubes by chemical and electrochemical reduction of as-prepared TNT layers [20–27]. It has been shown that black TNTs can be a promising material for supercapacitors, fuel cells, lithium-ion batteries, etc. [4,5,23,26,27]. It is also of interest to use black TiO_2 nanotubes as effective light-absorbing coatings [28]. An important advantage of light-absorbing TNT layers is the presence of an ordered porous structure with given pore size.

It is known that doping with carbon has a significant effect on the structure and photocatalytic activity of TiO_2 . In most investigations, carbon doping of TiO_2 is realized by specially developed methods, for example, by thermal treatment in the atmosphere with carbon-containing substances without oxygen access [4,11,17,20,29]. Previously, predominantly powdered $\text{TiO}_{2-x}\text{C}_y$ samples were studied, while the state of carbon and its effect on the properties of titania nanotubular layers when doped from organic components of an electrolyte used for electrochemical preparation of anodic TNTs have been less studied. It was shown that amorphous carbon is present in TiO_2 nanotubes grown in ethylene glycol electrolytes and then annealed in a hydrogen-containing atmosphere [5,22,23].

As is known, during valve metal anodizing, a side process such as electrolyte oxidation might proceed along with the main anodic process of metal oxidation. While the role of structural defects and dopants in changing the color and properties of titanium dioxide was well established, the role of carbon and other impurities (F, N) in the appearance of color and changes in the properties of anodic TiO_2 films was insufficiently studied [22,23]. The modification of anodic metal oxide films with the products of electrochemical oxidation of electrolyte components can create additional opportunities for tailoring the properties of materials [2,5,6,17,20–23].

This work is aimed at establishing the contribution of various substances and defects to the deep black coloration of TiO_2 nanotubular layers upon their annealing in an H_2 atmosphere. The nature of the paramagnetic defects in nanotubular titania films prepared by electrochemical oxidation of titanium in an ethylene glycol electrolyte and then annealed in H_2 was studied using the EPR method. To establish subtle structural differences, we also performed a comparative study of some non-black TNT samples annealed in air.

2. Materials and methods

Titanium plates ($4 \times 1 \text{ cm}^2$; 99.7% Ti, Alfa Aesar) were polished mechanically and then chemically in HF:HNO_3 (1:2 vol) mixture to mirror finish, and finally rinsed with deionized water. According to Ref. [30], self-organized, highly ordered nanotubular titania layers were produced by two-step anodization in EG containing 0.75% of NH_4F and 2 vol % of H_2O . The anodizing voltage was increased from 0 to 40 V with a sweep rate of 200 mV s^{-1} followed by a constant voltage process for 1 h. The oxide films formed during the first step of anodization were removed in an ultrasonic bath with deionized water. Before the second anodization, the electrochemical cell was filled with a fresh portion of the electrolyte. After the second step, the samples were washed with ethanol, and then their surface was cleaned from debris by treatment in an ultrasonic bath with distilled water for 30 s. To obtain crystalline TiO_2 nanotubes, the samples were annealed at 450 °C for 1 h in the air or at 500 °C for 1 h in hydrogen.

The size and morphology of the TiO_2 nanotubes were characterized by scanning electron microscopy (SEM) using a LEO 1420 microscope and transmission electron microscopy (TEM) using a LEO-906E microscope.

The EPR spectra were recorded at 77 and 298 K on a VARIAN E 112 spectrometer at 9.35 GHz (X -range). The power of the microwave radiation was varied from 0.2 to 64 mW; the amplitude of modulation was 0.05, 0.1, 0.2, and 0.4 mT at a modulation frequency of 25 kHz. The values of the g -factors and the concentration of paramagnetic centers (PCs) were determined relative to the reference samples: the g -factor relative to the position of the lines of hyperfine structure (HFS) of $\text{Mn}^{2+}/\text{MgO}$; the concentration of PCs (N_x) relative to a carbon standard.

EPR spectra were recorded directly from titanium plates with TiO_2 films deposited during the anodization process. The plates with a size of $(2.0 \pm 0.2) \times (7 \pm 1) \text{ mm}^2$ were placed in the resonator. The composition, treatment conditions, sample colors, and concentration of PCs with $g \sim g_e$ are listed in Table 1. It was found that the presence of non-anodized titanium did not affect the spectrum parameters. Titania films possess a highly ordered nanotubular structure with the inner TiNT diameter of $60 \pm 5 \text{ nm}$, the wall thickness of $12 \pm 2 \text{ nm}$, and layer thickness of $7 \pm 2 \mu\text{m}$ (Figs. 1 and 2). The size and morphology of the nanotubes do not change after annealing in different atmospheres. But untreated films were amorphous, while annealing in air at 450 °C and in hydrogen at 500 °C resulted in the formation of anatase phase [30].

Besides the bare titania nanotubular films, samples covered with gold were obtained using a colloidal solution of gold nanoparticles with an average size of 5 nm. According to Ref. [31], after adding colloidal gold, the samples were successively dried in a vacuum and heated at 200 °C for 1 h. Thus obtained films coated with Au were found to differ from the bare TiNT films by the electrocatalytic properties. In the present work, Au was introduced to the TiNTs in order to change their relaxation characteristics and, consequently, make it possible to register the EPR signals from Ti^{3+} ions and F -centers at 77 K. As is known, in crystallites with high symmetry, the signal from these centers can be registered at a very low temperature only (4 K). A decrease in the symmetry of the coordination surrounding can make it possible to record EPR spectra of titania at 77 K as a result of high non-stoichiometry or local lattice distortions caused by contact with the surface of Au nanoparticles [32]. The EPR spectrum of the A-12 graphene nanosized powder (GNP) (2 mg) was collected at 77 K using the microwave radiation power of 5 mW and the amplitude of modulation of 0.2 mT.

3. Results

3.1. The color of TiNT films

The color of TiNT films might give us some preliminary information on the nature of defects in the structure of titania. The films have different colors depending on the annealing conditions (See Table 1). As-anodized films are grey, which is characteristic of films with nanotubular structure. The films become blue after heat-treatment in air, which can be explained by their non-stoichiometry, i.e., the presence of

Table 1

Appearance, composition, color, and concentration of PCs with $g \sim g_e$ (EPR spectra were recorded at 77 K) of TiNTs obtained at 40 V in EG solution containing 0.75% NH_4F and 2 vol % H_2O .

Sample name	Composition	Annealing conditions	Color	$C_{\text{PC}} \times 10^{13}$, spin mm^{-2} (77 K)
1 (TiO_2/Ti)	TiO_2/Ti	As-anodized	Grey	-
2 ($\text{TiO}_2/\text{Ti450A}$)	TiO_2/Ti	450°C, air	Bluish	0.2
3 ($\text{Au}/\text{TiO}_2/\text{Ti450A}$)	$\text{Au}/\text{TiO}_2/\text{Ti}$	450°C, air	Blue	0.4
4 ($\text{TiO}_2/\text{Ti500H}$)	TiO_2/Ti	500°C, H_2	Black	20