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Transparent photocatalytic coatings on the surface of the tips of medical fibre-optic bundles

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Abstract. **We report the results of the development of the sol–gel method for obtaining thin, transparent (in the visible part of the spectrum) TiO_2/MgO coatings on the surfaces of the tips of medical fibre-optic bundles. Such coatings are capable of generating singlet oxygen under the action of UV radiation and are characterised by high antibacterial activity.**

Keywords: *photocatalytic and bactericidal properties, optical fibre, singlet oxygen.*

Currently, a large number of studies are aimed at developing materials that have photocatalytic properties. These properties of various powdered oxide materials have been studied in many works. However, the use of powders is not possible in products and devices when it is necessary to preserve their transparency. An example of devices, for which the formation of a transparent photocatalytic layer capable of generating singlet oxygen is highly topical, is the fibre-optic bundles which are increasingly used in medicine, in particular in oncology [1]. It is for such applications that the use of thin transparent photocatalytic coatings applied to the working surface of a product is promising.

The photocatalytic coatings under development are capable of generating singlet oxygen under the action of UV radiation (for example, under the action of sunlight) and decomposing photochemically the organic compounds and impurities on their surfaces. Titanium dioxide (TiO_2) represents the most common and efficient material for photocatalytic coatings [2, 3].

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The aim of this work is the development of a thin transparent photocatalytic coating to be applied to the surface of a tip of a medical fibre-optic bundle. Small thickness and low level of light absorption of the coating material being applied ensure the preservation of high transparency in the visible part of the spectrum of the fibre-optic bundle with a photoactive tip. At the same time, the transparency of optical fibres in the near-UV spectrum region is capable of allowing UV radiation to be transmitted along them to the photoactive tip and generating singlet oxygen in the immediate vicinity of the object of medical research.

In our work we used flexible regular fibre-optic glass bundles ('VOT' Ltd., St. Petersburg) which possess high transparency in the visible and near-UV spectrum regions. The bundles consisted of 50 single fibres with a diameter of 14.5 μm placed in a hermetic polymer cladding. The luminous diameter of the bundle was 1.6 mm, and its resolving power was 35 mm^{-1}. The tips of the fibre-optic bundles were thin plane-parallel glass plates with a diameter of 3 mm.

In papers [4, 5], two-component (TiO_2–SiO_2, TiO_2–P_2O_5, TiO_2–MgO) photocatalysts were studied, and it was shown that the introduction of SiO_2, MgO and P_2O_5 allows modifying the structure of TiO_2-coatings and changing their morphology and sorption properties. Therefore, in the present work, TiO_2 and MgO have been used as oxide materials for the formation of photocatalytic coatings.

For the formation of coatings, we used the sol–gel method. Tetraethoxytitanium, magnesium perchlorate, high-molecular-weight (M_w = 1300000) polyvinyl-pyrrolidone and a mixture of organic solvents were used as initial components for the film-forming solutions. The coating was applied by immersing the glass plates into the film-forming solutions, followed by their extraction and drying at a temperature of 80 °C for 24 hours. The dried plates were heated in a laboratory electric furnace at a temperature of 530 °C for 2 hours. The thickness of the formed oxide coatings constituted 200–250 nm.

Absorption spectra of the coatings were measured with a UV-3600 spectrophotometer (Shimadzu, Japan) in the wavelength range of 300–1000 nm, and luminescence spectra – with a SDH-IV spectrometer (SOLAR Laser Systems, Republic of Belarus). To excite the photoluminescence of the material, we used the emission of an HPR40E-50UV LED with an intensity maximum at λ = 370 nm.

Figure 1 shows absorption spectra of a glass tip without coating, and also that of a tip with the $0.67MgO-0.33TiO_2$

coating. It can be seen that the tip with the oxide coating is highly transparent throughout the visible spectral range (the transmittance *T* is about 85%–86%).

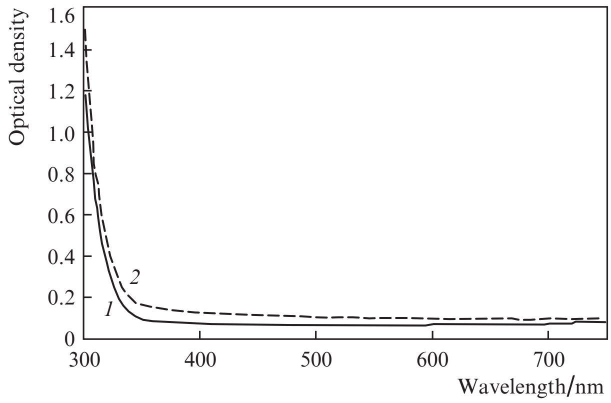

Figure 1. Absorption spectra of (*1*) a glass tip without coating and (*2*) a tip coated with 0.67MgO–0.33TiO_2.

Figure 2 shows the photoluminescence spectra (λ_{ex} = 370 nm) for the coatings based on TiO_2 and 0.67MgO–0.33TiO_2. A characteristic luminescence band of singlet oxygen with λ_{max} = 1270 nm corresponding to the electronic transition $^1\Delta_g - {}^3\Sigma_g$ is observed in the spectra [6]. This indicates the efficient generation by coatings of the chemically active singlet oxygen which plays an important role in photocatalytic processes.

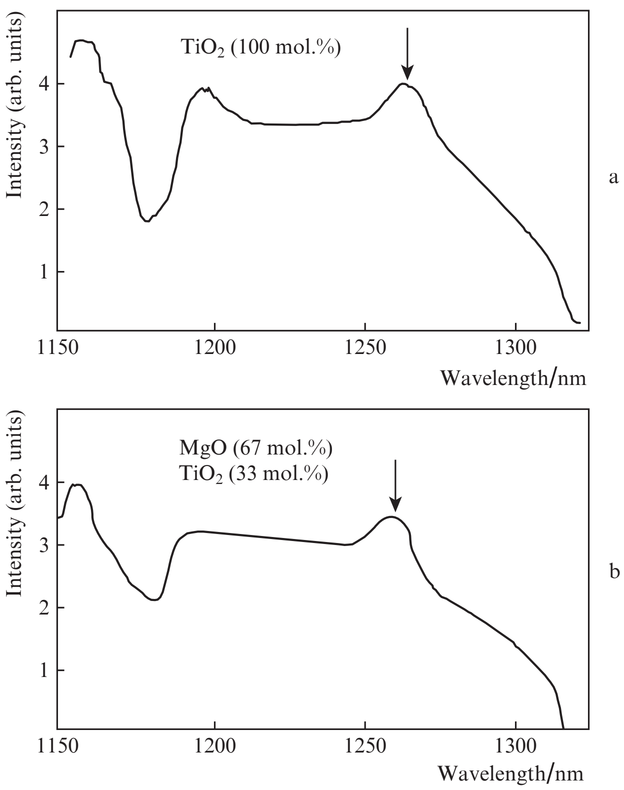

Figure 2. Photoluminescence spectra of (a) TiO_2 and (b) 0.67 MgO–0.33 TiO_2 coatings (λ_{ex} = 370 nm). The arrow indicates the luminescence band maximum of singlet oxygen.

According to the data of the electron microscopic analysis, the transparent coatings obtained on the surface of the glass tip consist of the uniformly sized (15–20 nm) densely packed oxide nanoparticles completely covering the glass surface (Fig. 3). The small size of oxide particles and their uniformity in size ensure high transparency of coatings.

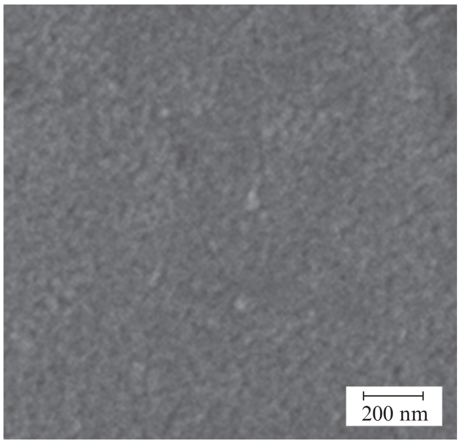

Figure 3. Image of the MgO/TiO_2 coating surface on a glass tip obtained with an electron microscope.

Figure 4 presents a diagram illustrating the construction and photoactive effect of a fibre-optic bundle with a transparent photocatalytic and bactericidal tip. Experiments have shown that the use of the tip with a thin TiO_2/MgO coating we have developed preserves high transparency of the fibre-optic bundle and also ensures the generation of singlet oxygen by the tip under the action of UV radiation propagating along the fibres with λ_{ex} = 370 nm.

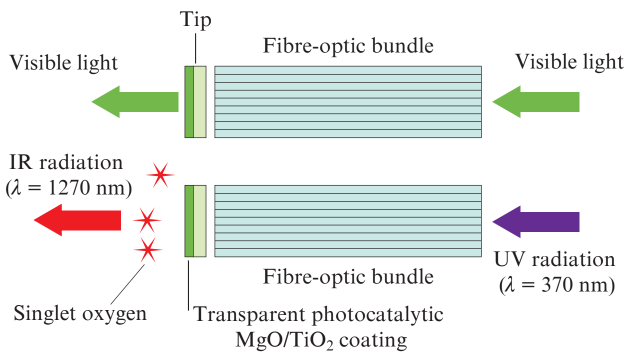

Figure 4. Scheme illustrating the construction and photoactive effect of a fibre-optic bundle with a transparent photocatalytic and bactericidal tip.

It should be noted that the use of fibre-optic bundles with photocatalytic tips in medicine is promising not only for research and diagnosis of diseases of internal organs, but also for active exposure with chemically active singlet oxygen. In the scientific and patent literature, such photocatalytic tips for fibre-optic bundles have not yet been described to date.

Thus, we have experimentally demonstrated the possibility of the developemnt of the fibre-optic bundles with a tip covered with an oxide layer of TiO_2/MgO capable of generating singlet oxygen under the action of UV radiation propagating through the fibres. The bactericidal coating on the tip is formed by the sol–gel method and is characterised by high transparency in the visible part of the spectrum.

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