PHOTOCATALYTIC GLASS FIBERS PREPARED BY SOL-GEL METHOD

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Abstract: *The maintenance and improvement of current properties and the creation of new material properties are the most important reasons for the functionalization of textiles. This work is aimed at the exploitation of the TiO_2 sol-gel method for its photocatalytic effect on glass fibers. The aim was to optimize the temperature of fixation prepared layers, and find the right concentrations of TiO_2 for the photocatalytic effect on ascorbic acid in solution as model chemicals.*
Key words: *photoctalytic, sol-gel, titanium dioxide.*

1 INTRODUCTION

Sol gel method

Under the abbreviation "sol gel method" is the proposed application of sol to fiber surfaces, where the sol will be changed into gel. The principle of the sol-gel method is the preparation of the homogeneous solution of fundamental components, which is then transferred into sol by controlled hydrolysis and polycondensation [1, 2]. This sol is deposited on the surface of materials, transferred into gel and finally onto a layer of oxide via heat treatment. The layer of oxide is nonporous and glassy or crystalline at higher temperatures of heat treatment. However, at lower temperatures of heat treatment it stays amorphous and porous. In production and for research purposes SiO_2 and TiO_2 layers are deposited most often. Also, layers of many other constitutions containing Al_2O_3, B_2O_3, ZrO_2, PbO and another oxide are usually prepared. Along with clearly inorganic layers, hybrid inorganic-organic layers are also developed (production terms ORMOCER, ORMOSIL and NANOMER) which contain chemical bonds of organic substances and functional groups next to silicon, titanium, zirconium and oxygen.

In the surface treatment of polymer structures it is necessary to use hybrid layers based on a mixture of inorganic and organic polymer compounds, which are joined, at the end of process, to one macromolecular network. The inorganic part is connected with chemical, mechanical and thermal stability. The organic part is works as a networking agent and increases the stability of layers against the chemicals selected. In some hybrid polymers, metal complex bonds are used to increase stability. These hybrid layers are able to stabilize at relatively low temperatures of about 100°C.

Preparing very thin layers (10 up to 500 nm thick) of composite nanomaterials is further possibility with this method [1].

Layers prepared by the sol-gel method are industrially used like reflex and antireflex layers in optics; protective, catalytic, modified and functional layers in material engineering; and functional layers in microelectronics and biotechnology [1, 2].

Changing surface materials properties is possible with deposition functional groups or with an inorganic top coat using the sol gel method. One of advantages of this method is the possibility to prepare thin layers on various materials. Up to now, mainly inorganic substrates (glass, ceramic, metals etc.) were used, however, thin layers can also be deposited on organic materials especially on polymers. Using this method it is possible to prepare TiO_2 layers with photocatalytic properties or coloured of substrates [2].

Photo-catalytic

Photo-catalytic is a photochemical reaction. The acceleration of this reaction is helped along by presence of catalyst. Photochemical reactions invite absorption of lights by materials, whose molecules are broken up by absorbed energy, ions or atoms.

Observing the photo activity of nano particle TiO_2 in real time is of scientific interest. Titanium dioxide belongs to the most used photo-catalysts. Photo-catalytic, an effect of TiO_2 by the instrumentality of UV radiation at the normal temperature, makes it possible for oxidative decomposing of organic structures, and also bacillus [3]. The result of these effects is the breakdown of all organic materials to elemental inorganic components.

Photo-catalytically reactions are exploited for cleaning of water and air. This technology is able to prevent the contamination of the outside wall of buildings, preventing the misting of frontal glass and driving mirrors of cars [4, 9-12].

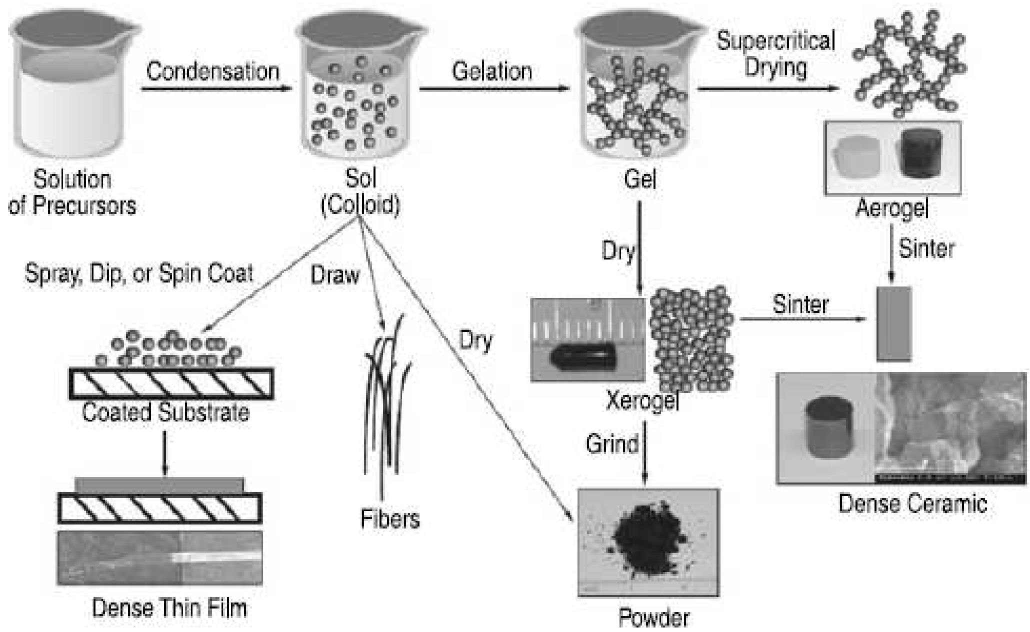

Figure 1 Steps of the sol-gel processing of materials and examples of the microstructure of final products. Bold-lined rectangles show possible final of the sol-gel method [7]

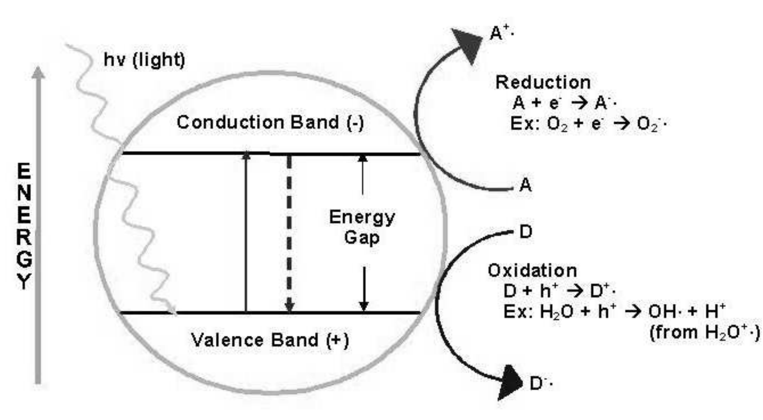

Figure 2 Schematic diagram of the mechanism for the photocatalytic action of nano-structured TiO_2 [8]

When a semiconductor, such as TiO_2 absorbs a photon of energy that is equal to or greater than its band gap width (Eg in case of TiO_2 amounts to 3.2 eV), an electron (e^-) may be promoted from the valence band (VB) to the conduction band (CB) thus generating an electron vacancy – ''hole'' (h).The electron and the hole can migrate to the catalyst surface where they participate in redox reactions with different species adsorbed on catalyst surface. Holes can react with surface-bonds H_2O or OH^- to produce the hydroxyl radical. Electrons, during a reaction with oxygen, can generate superoxide radical anion. The hydroxyl radicals (OH^-) and superoxide radical anions are supposed to be the primary oxidizing species in photocatalytic oxidation processes. These oxidative reactions could result in the degradation of an acid [6].

$$TiO_2 + hv \rightarrow e^-_{cb} + h^+_{vb} \quad (1)$$
$$h^+_{vb} + H_2O \rightarrow \bullet OH + H^+ \quad (2)$$
$$h^+_{vb} + OH^- \rightarrow \bullet OH \quad (3)$$
$$h^+_{vb} + R \rightarrow R^+ \quad (4)$$
$$e^-_{cb} + O_2 \rightarrow O_2\bullet^- \quad (5)$$

2 MATERIAL AND METHODS

2.1 Materials

Microfiber glass textile structure

The substrate used (Spepat-F, Czech Republic) was a laboratory filter material Z75, which was made from 100% glass microfibers. Areal density of the material used was 75 $g.m^{-2}$. Average diameter of fibers is about 1 μm.

Sol description

Sol TiO_2 is prepared on bases tetraisopropyl orthotitanate and isopropyl alcohol as solvent. Concentration of sol was 1.3 g TiO_2/100 g solution.

Ascorbic acid

Ascorbic acid was purchased from Lach-Ner,s.r.o., Czech Republic and used without further purification. Its structure is given in Figure 3.

Structure of ascorbic acid is relatively complicated and it contains some double bonds – this structure absorbs intensively light in UV light below 290 nm (Figure 3).

Aeroxide P25 (Degussa)

Degussa P25 is a fine crystalline powder without a smell; its specific surface area is 50±15 $m^2.g^{-1}$, and its moisture is ≤ 1.5 wt%. Degusa P25 has a composition structure of 70% anatase and 30% rutile.

Into the tested sol were added TiO_2 particles (Degussa P25) in concentrations of 1, 2, 5, 10, 15 and 20 $g.l^{-1}$.

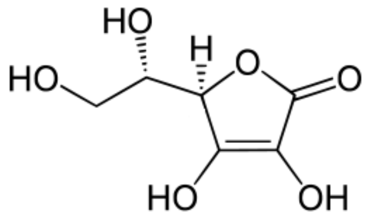

Figure 3 Structural formula of ascorbic acid

2.2 Methods

Sol-gel application

The concentration of titanium dioxide 1, 2, 5, 10, 15 and 20 $g.l^{-1}$ was dispersed into a 50 ml sol-gel solution. The TiO_2 layer was deposited on the material in with the stipple foulard method (W. Mathis, Switzerland) with a horizontal cylinder pressure at 4 bar and speed of pass 1 $m.s^{-1}$. The impregnated samples were dried at laboratory temperature for 20 min, and then for fixation at a temperature of 150, 250, 300 and 400°C in a drying machine (EPS, Czech Republic).

Measurement of photo-catalytic activity

Testing of photo-catalytic was based on oxymetr measuring. The dissolved oxygen was measured by Oxi 315i with sensor CellOx325. The quantity of oxygen in closed system is reduced by the photo-catalytic process in liquid system. This system was irradiated by UV light at 256 and 366 nm. The system is presented as Figure 4. Measured "photo - catalytical degree" is calculated from the rate of O_2 concentration decrease in the system during the test.

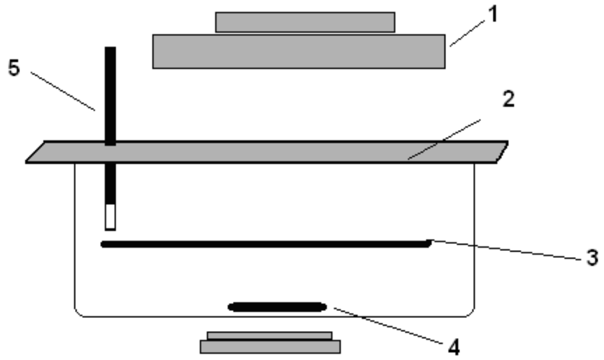

Figure 4 Schematic diagram of the experimental setup: (1) UV lamp; (2) polyethylene foil; (3) layer with TiO_2; (4) magnetic stirrer; (5) sensor CellOx325

The closed system contains a water solution of model chemicals, of dissolved oxygen, photocatalytic TiO_2 and an oxymetr sensor. The total volume of water in this apparatus is 1000 ml. The impregnated samples were dried at laboratory temperature for 20 min, and then for fixation at a temperature of 150, 250, 300 and 400°C in a drying machine (EPS, Czech Republic). The homogeneity of the system is supported by magnetic stirring (300 rotations per minute). The experimental arrangement is visualized in Figure 5.

The system was irradiated by a UV lamp (P-Lab a.s., Czech Republic). The light source used is alight tube with an input of 8 W with a light emission of 366 nm. The distance between the light tube and tested solution was 20 mm. Every 2 minutes the concentration of oxygen in the system was measured. The temperature was 19°C for standard experiments. Between the UV light source and the closed system is placed the transparent polyethylene foil (Chemosvit a.s, Slovak Republic, thickness 30 μm, area weight 27.6 $g.m^{-2}$). This foil reduces the transport of oxygen between the air and closed system to zero. Polyethylene foil cannot absorb any UV light with a wavelength above 220 nm. The mechanic properties of foil help to easily close the system.

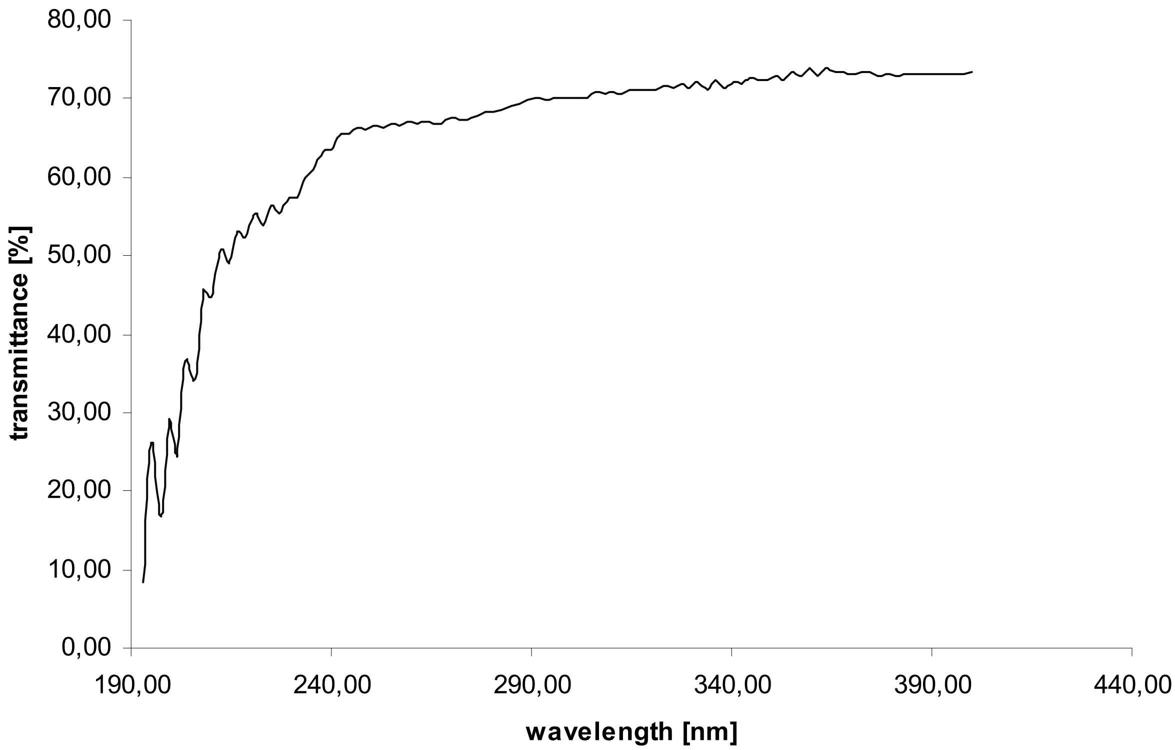

Figure 5 Absorption spectrum of used polyethylene foil

Principle of measurement: The quantity of oxygen diminishes in a closed system. In the closed system there should by a solution of model chemicals, which will be oxidized by oxygen activated by photocatalys. In all of the experiments was used ascorbic acid in concentration 0.1 gl^{-1}.

3 RESULTS AND DISCUSSION

The photocatalytic effect was measured for all prepared textile samples. The results are collected in Figure 6.

The layer without TiO_2 nanoparticles is inactive. The increased content of TiO_2 particles in the layer is connected with the increase of photoactivity. The optimal content of TiO_2 particles in optimal heated layer is about 5 $g.l^{-1}$ of sol.

The influence of sol-gel fixation on temperature is important, but the interpretation of results is not easy. At low fixation temperatures (150 and 250°C) we can find more porous layers, the particles in the layer are active in high concentration, leading to the release of TiO_2 particles in solution, increase of TiO_2 surfaces in solution and thereby increasing the photocatalytic effect. At higher temperatures (300 and 400°C) the structures of layers are more stabilized by the reduction of surface area and destruction of organic compounds in the gel. The samples fixed at higher temperatures are mechanically more stable.

In the pictures from electron microscopy we can see changes in the textile structure. The original fibers are in the Figure 7, individual fibers are not connected to other fibers, and the surfaces are clean.

On the following Figures 8 and 9 are compared the fibres structures with different quantity of TiO_2 particles in layers. The samples with low quantity of particles (1 or 2 $g.l^{-1}$) are covered by relatively even layer of particles on each surface. The samples with very high quantity of particles (15 or 20 $g.l^{-1}$) are covered by relatively even layer of particles, but the considerable part of particles is fixed in large aggregates with size about 2 μm. These relatively large particles are probably low photo-active, because the photocatalyses is only on the accessible surfaces.

Utilizing theTiO_2 based sol gel technique is useful for glass fibers. The fibers are covered by an even layer and only in some crossing of fibers can we observe the layer connecting fiber together. In Figure 10 it is possible to see the film cracking because of thermal stress.

In this work was not used any the test for a proof the bonds. But you can expect that the bonds are of a physical character.

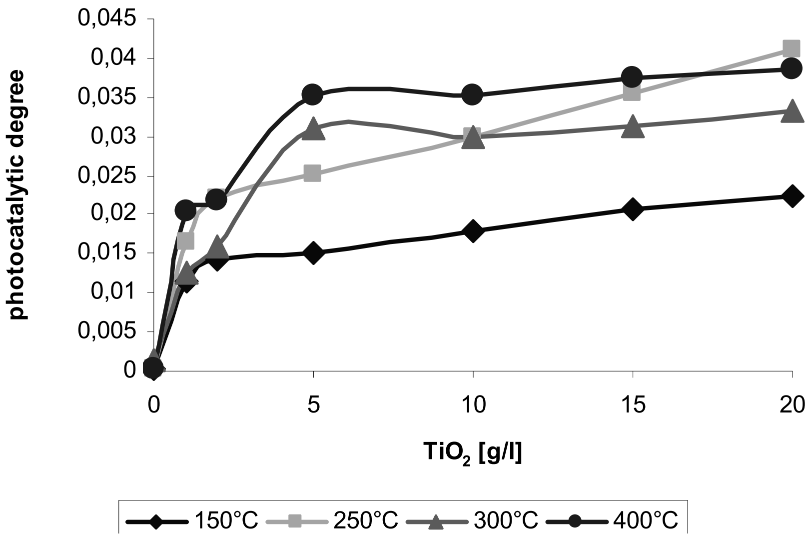

Figure 6 Dependence of the concentration of TiO_2 particles on the degree of fixation at different temperatures

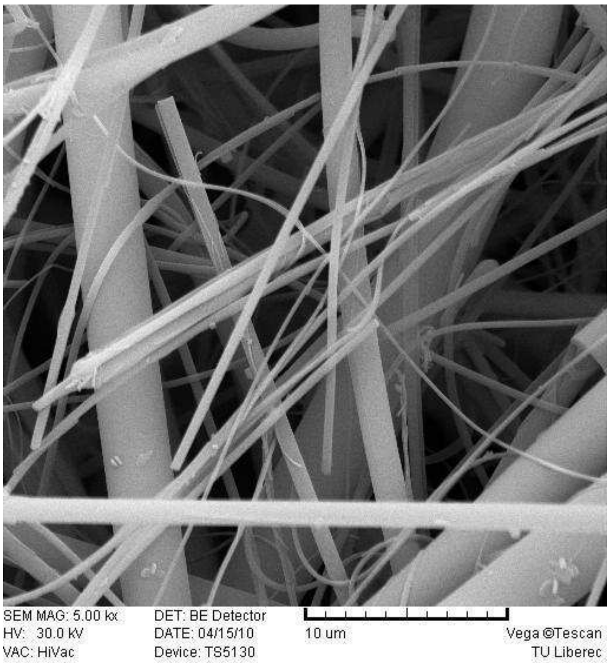

Figure 7 Original fibres

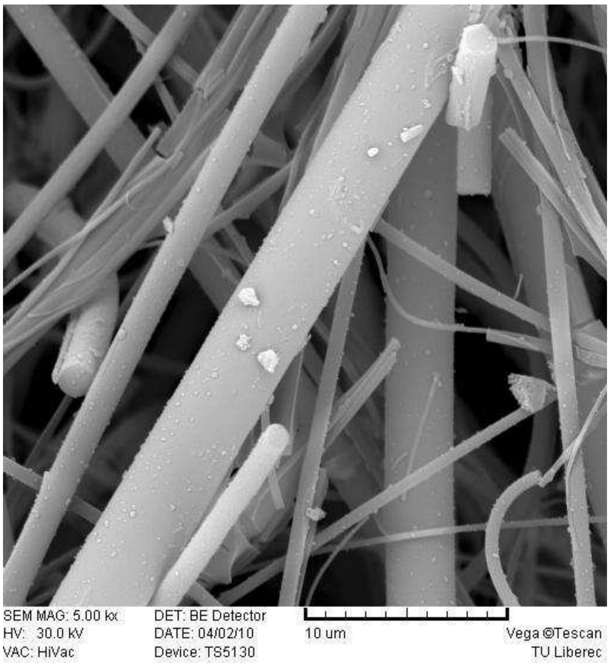

Figure 8 150°C, 2 g.l^{-1} – example of balanced coverage of fiber particles at low particle concentration

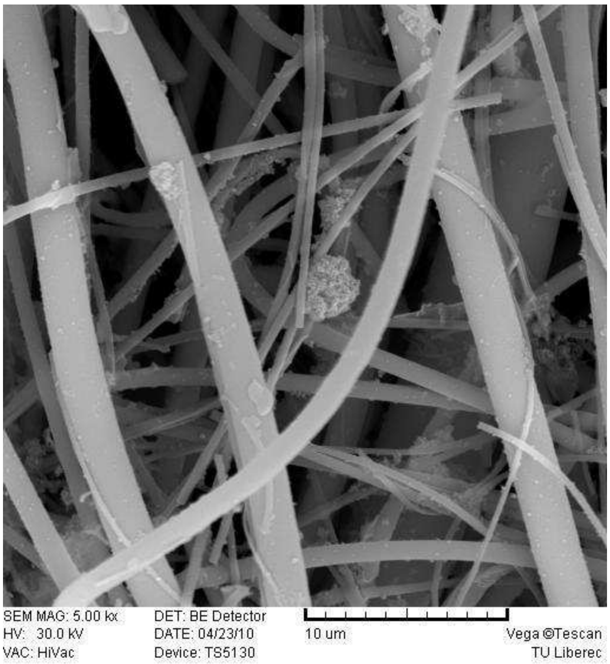

Figure 9 150°C, 20 g.l^{-1} – example of uneven coverage of fibers and particles, creating clumps of particles at high particle concentration

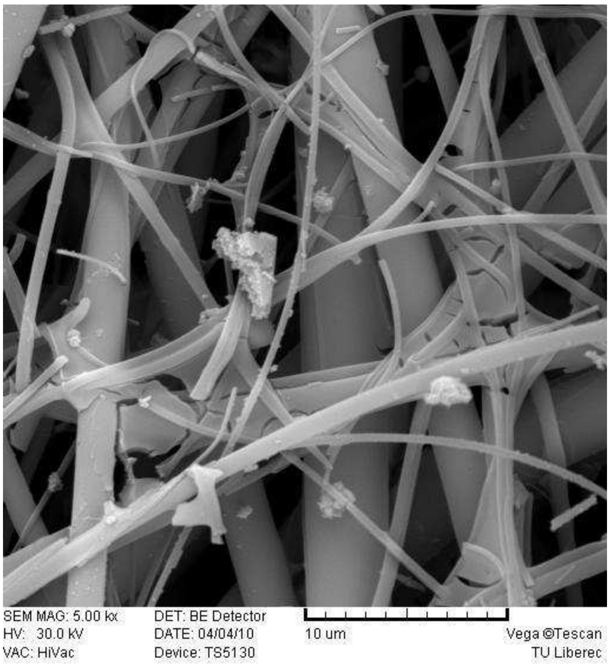

Figure 10 Combination of fiber and film cracking due to stress

4 CONCLUSIONS

TiO_2 layers are interesting holders of TiO_2 particles for the purpose of obtain high photocatalytic properties on textile structures. The optimal concentration of TiO_2 particles was in our case 5 g of Degussa P25 particles in one liter of sol. The optimal temperature of stabilization is 400°C – the prepared layers are mechanically stable and the layers are intensively photoactive.

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FOTOKATALYTICKÁ SKLENĚNÁ VLÁKNA PŘIPRAVENÁ METODOU SOL-GEL

Translation of the article
Photocatalytic glass fibers prepared by sol-gel method

Článek se zabývá využitím ukotvení TiO_2 částic pomocí sol-gel metody na skleněná vlákna a využitím fotokatalytického účinku těchto vláken. Cílem práce bylo optimalizovat teplotu fixace sol-gel vrstvy a najít správnou koncentraci TiO_2 pro fotokatalýzu. Ta byla testována na kyselině askorbové, která sloužila jako modelová látka při stanovení oxymetrickou metodou.