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# Synthesis and properties of photocatalytic active composite materials based on $\text{TiO}_2$ and modified by Ag and $\text{SiO}_2$

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**Abstract.** Nowadays air and water pollutions are becoming a serious problem for urban environment. One of the efficient methods of purifying water and air is photocatalysis on  $\text{TiO}_2$  films. In this work, we obtained composite materials based on  $\text{TiO}_2$  and modified by Ag and  $\text{SiO}_2$  on the surface of the fiberglass material ( $\text{Ag/SiO}_2/\text{TiO}_2/\text{FGM}$ ) by a sol-gel method. Complex studies were carried out to identify the phase compositions, morphology and textural characteristics of obtained samples by X-ray diffractometry, scanning electron microscopy, micro-X-ray spectral analyses and analysis of  $\text{N}_2$  adsorption-desorption isotherms. Surface area and average pore size of this sample is  $8.2 \text{ m}^2/\text{g}$  and  $11.4 \text{ nm}$  respectively. Prepared composite  $\text{Ag}(0.5\%)/\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$  material revealed photocatalytic activity in model reaction of methyl orange azo dye photodegradation under UV-irradiation.

## 1. Introduction

Titanium dioxide ( $\text{TiO}_2$ ) is one of the widely used semiconducting metal oxides. Titanium dioxide exhibits unique physicochemical properties such as close thermodynamic parameters of polymorphic structures, high strength Ti-O bonds, relatively low cost, non-toxicity, chemical stability, stable optical properties. These advantages make materials based on  $\text{TiO}_2$  very attractive for researchers. Polyfunctional materials based on titanium dioxide are promising candidates for application as self-cleaning surfaces, solar and fuel cells, protective and optical coatings [1].

The photocatalytic activity of  $\text{TiO}_2$  is one of its most interesting features. Photocatalysis is a recognized highly efficient method of purifying water and air, which has obvious advantages over traditional methods, including chlorination. Scientists all over the world are actively searching the effective photocatalytic materials, which can become a key to important environmental problems, including the elimination of organic pollutants contained in sewages. Nowadays filters based on  $\text{TiO}_2$  powders are used for photocatalytic purification of water and air from toxic organic impurities [2, 3]. Thin films based on  $\text{TiO}_2$  also can be used as photocatalyst [4]. The photocatalytic activity of  $\text{TiO}_2$  is largely determined by properties such as specific surface area, porosity, degree of crystallinity and the ratio of anatase and rutile crystalline phase [5]. One of the route to change these characteristics and improve photocatalytic activity is realized by addition of the other metal such as Ag [6–8].

The sol-gel synthesis using film-forming solutions (FFS) is one of the recognized methods to obtain functional composite oxide films with the required properties [9]. In this technique, the properties and composition of the initial sol significantly influence the obtaining of uniform oxide coatings. In the previous work [1] was shown that fiberglass materials of silicate origin are promising materials as a substrate for deposition  $\text{TiO}_2$  film. However, to create a homogeneous coating of  $\text{TiO}_2$  is



difficult, because fiberglass is hydrophobic. It was found, that the introduction of tetraethoxysilane into the sol composition made it possible to obtain uniform oxide coatings on substrates of various types [10, 11]. Moreover, it has been reported, that the presence of silica in  $\text{SiO}_2\text{-TiO}_2$  materials contributes to the formation of the anatase phase [12].

In the present study, composite  $\text{Ag/SiO}_2\text{/TiO}_2$  coatings on the surface of the fiberglass were prepared and thoroughly characterized. The prepared material revealed a catalytic activity in a model reaction of methyl orange oxidation under UV irradiation.

## 2. Experimental part

### 2.1. Materials and experimental procedure.

A fiberglass material (FGM) manufactured by JSC “Stekloplastik” (Russia) was used [1]. The composite  $\text{Ag/SiO}_2\text{/TiO}_2\text{/FGM}$  materials on the fiberglass were prepared using sol-gel method. At the first stage, to prepare the film-forming solution, three components were mixed: butanol-1 (99.9%, Ekos-1, Russia) as a solvent, bidistilled water as an initiator of alkoxide hydrolysis reaction, and  $\text{HNO}_3$  (UralPromDelivery, Russia). After, the tetrabutoxytitanium (TBT, extrapurity, Acros, USA), (TEOS, extrapurity, Ekos-1, Russia) and  $\text{AgNO}_3$  (99.9%, LenReactive, Russia) were added to the  $\text{C}_4\text{H}_9\text{OH-H}_2\text{O-HNO}_3$  mixture. The content of  $\text{AgNO}_3$  and TEOS was based on the need to obtain composite  $\text{TiO}_2\text{/FGM}$ ,  $\text{Ag}(0.5\%)\text{/TiO}_2\text{/FGM}$ ,  $\text{Ag}(1\%)\text{/TiO}_2\text{/FGM}$ ,  $\text{Ag}(1.5\%)\text{/TiO}_2\text{/FGM}$ ,  $\text{Ag}(2\%)\text{/TiO}_2\text{/FGM}$ ,  $\text{SiO}_2(1\%)\text{/TiO}_2\text{/FGM}$ ,  $\text{SiO}_2(2\%)\text{/TiO}_2\text{/FGM}$ ,  $\text{SiO}_2(3\%)\text{/TiO}_2\text{/FGM}$ ,  $\text{Ag}(0.5\%)\text{/SiO}_2(3\%)\text{/TiO}_2\text{/FGM}$  materials, respectively (in the work molar percentages are given). Freshly prepared solutions were kept at room temperature for three days. At the second stage, the deposition of film-forming solutions on the surface of fiberglass substrate was performed by impregnation technique. Thermal treatment was performed in two stages: drying at  $60\text{ }^\circ\text{C}$  for 1 h and calcination at  $600\text{ }^\circ\text{C}$  for 1 h at a heating rate of the muffle furnace  $5\text{ }^\circ\text{C/min}$ . The calcination temperatures of samples were chosen using previous studies [10, 11] and literature [13] data.

### 2.2. Research methods.

The morphology of the prepared samples was investigated by scanning electron microscopy (SEM) on a TM-3000 (Hitachi, Japan) operated at an accelerating voltage of 15 kV. The X-ray microanalyzer (Shift ED 3000) was used for energy-dispersive X-ray (EDX) spectroscopic analysis.

The phase composition of the samples was determined by X-ray diffraction (XRD) on a Rigaku MiniFlex 600 diffractometer (Japan) with  $\text{CuK}\alpha$  source in the range of reflection angles ( $2\theta$ ) from  $10$  to  $80^\circ$ . Interpretation of the obtained XRD patterns of samples was performed using the international data bank PDF-2.

BET surface area, pore volume and pore size distribution was determined by  $\text{N}_2$  adsorption-desorption method using a TriStarII automatic gas-adsorption analyzer and Micromeritics3Flex(USA) instrument. Prior to adsorption-desorption measurements, the samples were degassed for 2 h at  $200\text{ }^\circ\text{C}$  in a vacuum ( $10^{-2}\text{Torr}$ ).

Prepared materials after calcination were used as photocatalyst for the model reaction of methyl orange azo dye photodegradation. Stock solution methyl orange was prepared by dissolving required amount of methyl orange in distilled water (concentration  $1.5 \cdot 10^{-4}\text{ mol/L}$ ). For all the experiments, photocatalysts with the same size were added to 50 ml aqueous methyl orange. Then the reactor was irradiated by UV light with a radiation power of  $20\text{ mW/cm}^2$ . All the experiments were performed in presence of air at atmospheric pressure and constant magnetic stirring condition. The concentration of the dye was monitored directly in course of the photocatalytic reaction by use photoelectric concentration colorimeter, at a wavelength of  $\lambda = 463\text{ nm}$ . Measurements were performed every 30 min. Resulting dependencies of dye concentration on the duration of UV-irradiation were used further as a measure of photocatalytic activity of samples.

### 3. Results and Discussion

The structure parameters for all prepared materials are presented in Table 1. Pure fiberglass is a non-porous system with very low surface area ( $0.3 \text{ m}^2/\text{g}$ ) as reported in the previous work [1]. Deposition of  $\text{TiO}_2$ ,  $\text{SiO}_2/\text{TiO}_2$ ,  $\text{Ag}/\text{TiO}_2$  and  $\text{Ag}/\text{SiO}_2/\text{TiO}_2$  on fiberglass surface results in increase in pore volume. The presence of a hysteresis loop in nitrogen adsorption-desorption isotherms indicates the presence of mesopores in these samples. According to the results of the BET study all the samples have low surface area since fiberglass is the main component.

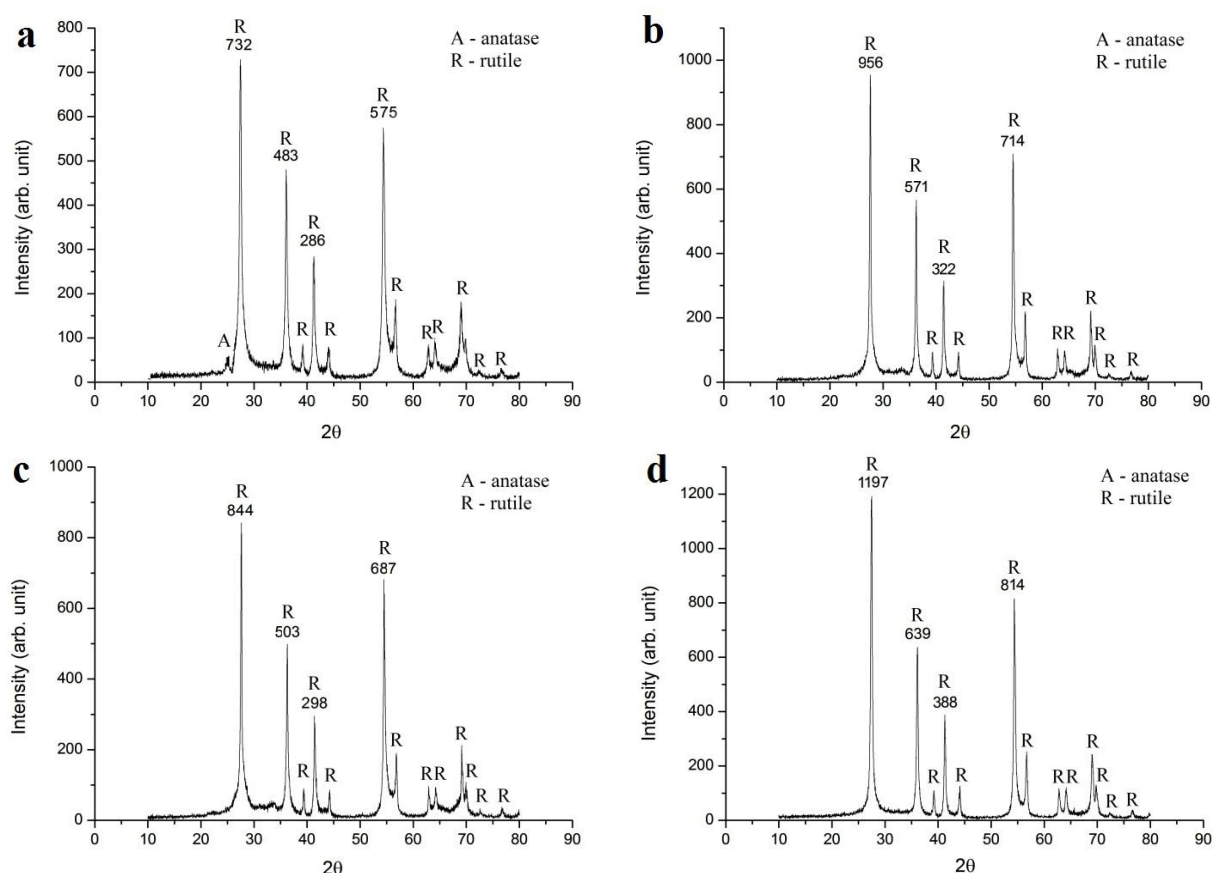
The increase of Ag content leads to decrease the surface area from  $7.9$  to  $6.6 \text{ m}^2/\text{g}$ , total pore volume and average size of composite  $\text{Ag}/\text{TiO}_2/\text{FGM}$  materials (Table 1). The maximum of structural parameters are observed for  $\text{Ag}(0.5\%)/\text{TiO}_2/\text{FGM}$  sample. The surface area, total pore volume and average size of  $\text{SiO}_2/\text{TiO}_2/\text{FGM}$  materials increases with the growth of  $\text{SiO}_2$  content. The maximum value of structural parameters are observed for  $\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$  sample (Table 1). According to the results of the BET study (Table 1) the composite material based on  $\text{TiO}_2$  and modified  $\text{SiO}_2(3\%)$  and  $\text{Ag}(0.5\%)$  on the fiberglass was chosen for future investigation. The specific surface area of the  $\text{Ag}/\text{SiO}_2/\text{TiO}_2/\text{FGM}$  sample is  $8.2 \text{ m}^2/\text{g}$ , that is 27 times higher than that of pure fiberglass.

**Table 1.** Structural properties of composite materials.

Composition	Average poresize, nm	Total pore volume, $\text{cm}^3/\text{g}$	$S_{\text{BET}}$ , $\text{m}^2/\text{g}$
$\text{TiO}_2/\text{FGM}$	11.21	0.27	8.3
$\text{Ag}(0.5\%)/\text{TiO}_2/\text{FGM}$	10.16	0.22	7.9
$\text{Ag}(1\%)/\text{TiO}_2/\text{FGM}$	9.67	0.18	7.1
$\text{Ag}(1.5\%)/\text{TiO}_2/\text{FGM}$	7.43	0.14	6.6
$\text{Ag}(2\%)/\text{TiO}_2/\text{FGM}$	8.36	0.17	7.4
$\text{SiO}_2(1\%)/\text{TiO}_2/\text{FGM}$	12.23	0.31	8.8
$\text{SiO}_2(2\%)/\text{TiO}_2/\text{FGM}$	13.88	0.36	9.1
$\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$	14.82	0.42	9.5
$\text{Ag}(0.5\%)/\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$	11.44	0.29	8.2

Figure 1 presents the XRD patterns of prepared samples. XRD patterns of all composites are characterized by intense and narrow reflexes indicating a high crystallinity of the samples. The XRD pattern of  $\text{TiO}_2$  clearly shows well resolved and sharp peaks at  $25.29^\circ$  and  $27.54^\circ$ ,  $37.93^\circ$ ,  $41.35^\circ$ ,  $54.53^\circ$  which confirm the presence of two different crystalline phases: anatase (tetragonal) and rutile (tetragonal) (PDF-2 Map No. 00-21-1276). The XRD patterns of  $\text{SiO}_2/\text{TiO}_2/\text{FGM}$ ,  $\text{Ag}/\text{TiO}_2/\text{FGM}$  and  $\text{Ag}/\text{SiO}_2/\text{TiO}_2/\text{FGM}$  samples have a similar appearance (Figure 2). X-ray analysis of these samples showed the absence of signals related to anatase and the presence of the main peaks at  $27.54^\circ$ ,  $37.93^\circ$ ,  $41.35^\circ$ ,  $54.53^\circ$  corresponding to rutile structural phase. It should be noted that for  $\text{TiO}_2$  samples, the intensity of main signal related to rutile is 732 a.u. at an angle of  $2\theta = 41.35^\circ$ . The intensity of this peak for  $\text{Ag}(0.5\%)/\text{TiO}_2/\text{FGM}$  (Figure 3),  $\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$  (Figure 4) and  $\text{Ag}(0.5\%)/\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$  composites are 956, 844 and 1197 a.u. respectively. This confirms that addition of  $\text{SiO}_2$  and Ag contributes to formation of titanium dioxide in the rutile modification.

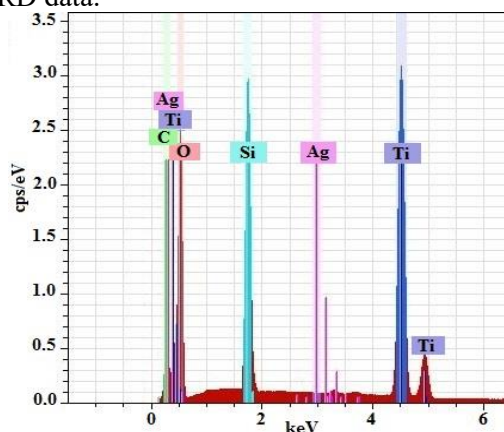
The XRD patterns of  $\text{SiO}_2/\text{TiO}_2/\text{FGM}$ ,  $\text{Ag}/\text{TiO}_2/\text{FGM}$  and  $\text{Ag}/\text{SiO}_2/\text{TiO}_2/\text{FGM}$  samples showed no peaks that can be attributed to the silver or silicon dioxide. We suggest that  $\text{SiO}_2$  and Ag content is below the instrument detection limit (less 5 wt. %).



**Figure 1.** XRD patterns of samples:

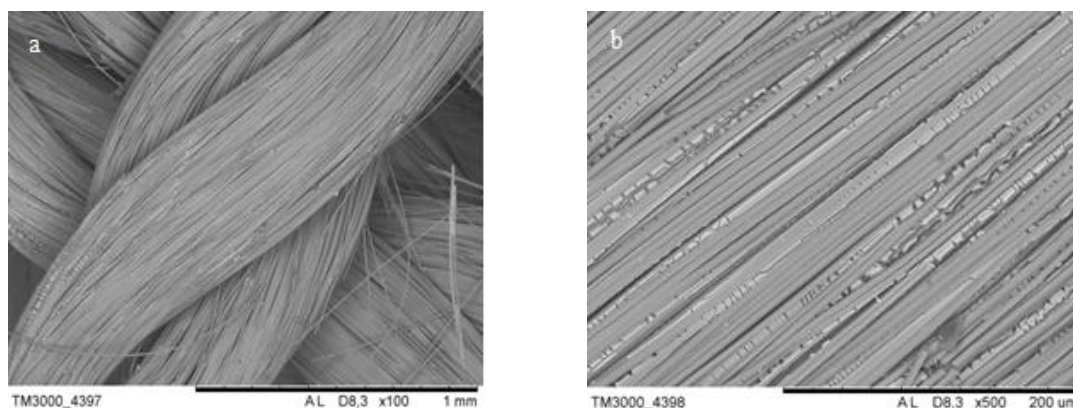
a –  $\text{TiO}_2/\text{FGM}$  ; b –  $\text{Ag}(0.5\%)/\text{TiO}_2/\text{FGM}$  ;  
c –  $\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$  ; d –  $\text{Ag}(0.5\%)/\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$ .

The results of a qualitative (Figure 2) X-ray spectral microanalysis confirm the presence of the the silver and silicon in the composition of final  $\text{TiO}_2/\text{SiO}_2(3\%)/\text{Ag}(0.5\%)/\text{FGM}$  sample. According to previous studies [10, 11], literature [13] and obtained results of EDX analysis, we assume the formation of Ag and  $\text{SiO}_2$ . The results of the quantitative EDX analysis show that the content of silicon compound in the obtained sample is less than 3 wt. % and silver content is less than 1 wt.%. This result agrees with the XRD data.



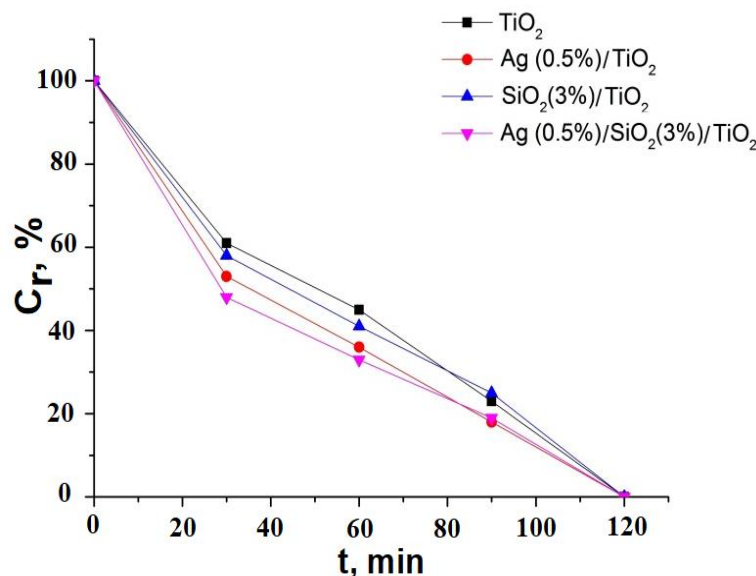
**Figure 2.** EDX images of  $\text{Ag}(0.5\%)/\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$  sample.

SEM images of  $\text{TiO}_2/\text{FGM}$ ,  $\text{SiO}_2/\text{TiO}_2/\text{FGM}$ ,  $\text{Ag}/\text{TiO}_2/\text{FGM}$  and  $\text{Ag}/\text{SiO}_2/\text{TiO}_2/\text{FGM}$  samples have a similar appearance. The morphology of the obtained composite  $\text{Ag}/\text{SiO}_2/\text{TiO}_2/\text{FGM}$  material is presented in Figure 3. It can be seen that the composite is attached to the surface of glass fibers. Each fiber is covered by  $\text{Ag}/\text{SiO}_2/\text{TiO}_2$  films. As shown in Figure 3,  $\text{Ag}/\text{SiO}_2/\text{TiO}_2$  film was not uniformly. There are some regions with cracks.



**Figure 3.** SEM images of  $\text{Ag}(0.5\%)/\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$  sample:  
a – magnification x100; b – increase x500

Methyl orange was used as a representative organic pollutant to evaluate the photocatalytic activity of the prepared composites. Figure 6 represents the photodegradation of methyl orange as a function of irradiation time over different samples.



**Figure 4.** Changes in the concentration of methyl orange in time on photocatalysts.

After the UV irradiation for 30 min, the photodegradation of methyl orange on  $\text{TiO}_2/\text{FGM}$  sample was 40%. Photodegradation of the dye on the modified samples proceeds more efficiently. For the  $\text{Ag}(0.5\%)/\text{SiO}_2(3\%)/\text{TiO}_2/\text{FGM}$  sample the photodegradation efficiency reached 50% for the same period of illumination. Solutions were completely discolored after the irradiation for 2 hours.

#### 4. Conclusion

The immersion of fiberglass material in the film-forming solution prepared by tetrabutoxytitanium, tetraethoxysilane, silver nitrate, and butanol, and subsequent heat treatment resulted in formation of the composite Ag/SiO<sub>2</sub>/TiO<sub>2</sub>/FGM materials. The formation of TiO<sub>2</sub> phases and presence of the Ag and SiO<sub>2</sub> phases were confirmed by X-ray powder diffraction data and qualitative X-ray spectral microanalysis. XRD confirmed that the addition of SiO<sub>2</sub> and Ag contributes to formation of titanium dioxide in the rutile modification. It was shown that each glass fiber was covered by composite Ag(0.5%)/SiO<sub>2</sub>(3%)/TiO<sub>2</sub>/FGM film, which led to an increase in the total surface area of material from 0.3 to 8.2 m<sup>2</sup>/g, and the appearance of pores with an average size of 11.4 nm. Prepared composite Ag(0.5%)/SiO<sub>2</sub>(3%)/TiO<sub>2</sub>/FGM materials revealed photocatalytic activity in model reaction of methyl orange azo dye photodegradation under UV-irradiation and showed the best degradation effect among Ag/TiO<sub>2</sub>/FGM, SiO<sub>2</sub>/TiO<sub>2</sub>/FGM and unmodified TiO<sub>2</sub>/FGM samples. Obtained results confirm promising use of composite Ag/SiO<sub>2</sub>/TiO<sub>2</sub>/FGM materials as photocatalyst.

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