

## One-stage Synthesis of Thermally Stable Nano-anatase with High Photocatalytic Activity

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Anatase nano-powder (TSP) was synthesized by annealing of peroxide-treated titanyl sulfate hydrate at 800°C. The product and intermediates (prepared at lower temperatures) were characterized by X-ray powder diffraction and IR spectroscopy. Their photocatalytic activity was studied in the model reaction of Methyl Orange degradation under UV irradiation. The properties of so-made samples were compared to the properties of the products of annealing naked titanyl sulfate hydrate under similar conditions (TS). Photocatalytic activity of the TSP samples is higher than photocatalytic activity of TS and commercial anatase Hombikat UV100, which is manufactured by pyrolysis of naked titanyl sulfate.

**Keywords:** Anatase, Photocatalysis, Annealing, Peroxide, Methyl Orange degradation, UV irradiation, Titanyl sulfate, X-ray powder diffraction, IR spectroscopy.

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### 1. INTRODUCTION

Nano-titania is now the most applicable heterogeneous photocatalyst. Among three natural modifications of TiO<sub>2</sub>, the highest photocatalytic activity was found for anatase. However, it is a metastable modification of TiO<sub>2</sub>, transforming at 700–800°C to the most stable rutile with lower photocatalytic activity. Therefore, the main methods of producing pure nano-anatase are based on low-temperature processes (sol-gel, reverse micelles, etc.) including numerous stages, such as solvolysis of an initial reagent, preparing of colloidal titania, transformation of sol to gel or powder, gel peptization or powder re-dispersion.

One of the simplest methods includes 5 stages and elongates for 26 h [1]. Its disadvantages are: the laboriousness of producing, low yield and variable parameters of the product.

For commercial production of nano-anatase, e.g. Hombikat UV100 (Sachtleben), titanyl sulfate is pyrolyzed at 300–600°C [2]. Higher temperature, which could increase titania crystallinity, is impossible due to thermal instability of anatase.

Thermally stable anatase was prepared by annealing amorphous titania, which was pre-transferred to a colloidal state with the H<sub>2</sub>O<sub>2</sub> solution, at 900°C [3]. Under the same conditions, but without H<sub>2</sub>O<sub>2</sub>, rutile formed. However, the method is also multi-staged.

We have combined these two methods in the synthesis of TiO<sub>2</sub> by annealing titanyl sulfate hydrate, pre-treated with concentrated aqueous solution of H<sub>2</sub>O<sub>2</sub>, at 800°C.

The purpose of the work was to optimize high-temperature method of preparing nano-titania by annealing H<sub>2</sub>O<sub>2</sub>-treated and untreated TiOSO<sub>4</sub>·2H<sub>2</sub>O at various temperatures.

### 2. EXPERIMENTAL

#### 2.1 Synthesis

The TiOSO<sub>4</sub>·2H<sub>2</sub>O powder (technical, Sigma Aldrich) was used as an initial reagent. Its X-ray diffraction pattern is shown in Fig. 1.

Nano-powdered samples (TSP) were prepared by cold impregnation of TiOSO<sub>4</sub>·2H<sub>2</sub>O with 30% aqueous solution of H<sub>2</sub>O<sub>2</sub> followed by annealing (in air) for 1 h at 250, 550 and 800°C (samples TSP250, TSP550 and TSP800, respectively). For comparison, a series of TS samples was prepared in similar conditions without treatment with H<sub>2</sub>O<sub>2</sub> (TS250, TS550 and TS800, respectively).

#### 2.2 Characterization

All the samples were characterized by X-ray diffraction (XRD) patterns, which were recorded with sample rotation on an HZG-4 (Ni filter) diffractometer: CuK<sub>α</sub> radiation in the diffracted beam, stepwise mode (counting time 10 s, a step of 0.02°).

IR spectra were recorded with an Infracum FT-02 spectrometer in nujol. The samples of initial reagents (and nujol) were pre-cooled at –21°C.

Electronic absorption spectra were recorded with an Aquilon CF 103 UV/vis spectrophotometer.

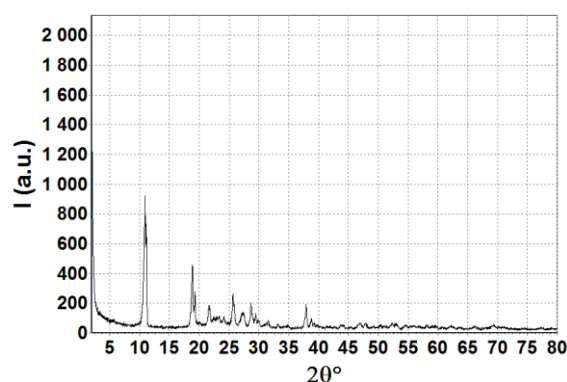
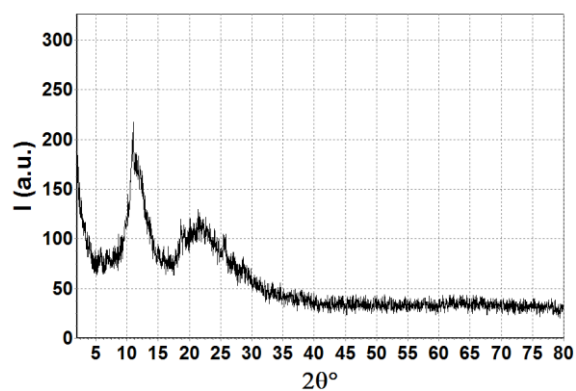


Fig. 1 – XRD pattern for TiOSO<sub>4</sub>·2H<sub>2</sub>O (technical, Sigma Aldrich)

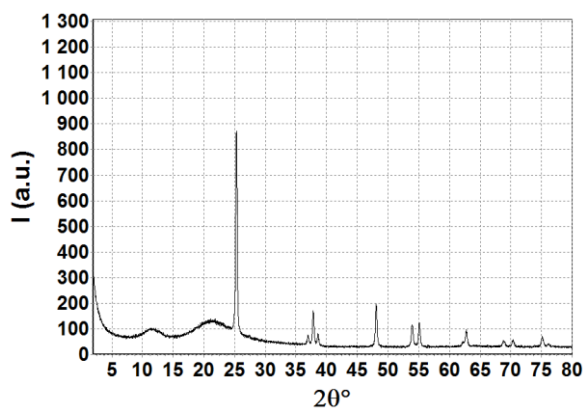
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a



b

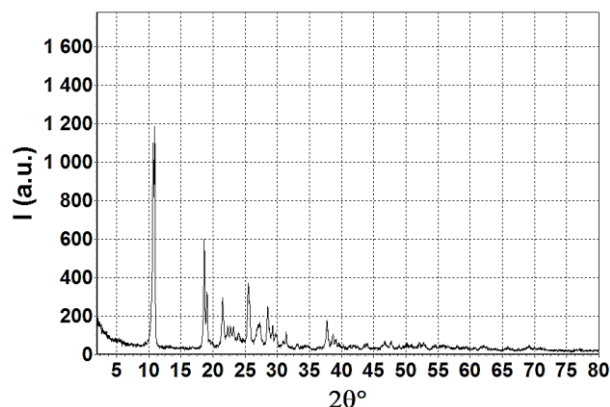
Fig. 2 – XRD patterns for TSP250 (a) and TSP800 (b)

Properties of samples were studied in the model reaction of photocatalytic degradation for color removal from aqueous solution containing organic dye Methyl Orange (4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt, MeO) under UV radiation (DRT-125 mercury lamp,  $\lambda = 250\text{--}400$  nm) in a photoreactor system with continuous stirring. The MeO dye degradation was monitored by absorbance at  $\lambda = 495\text{--}515$  nm or  $450\text{--}470$  nm (pH  $\sim 3$  or pH  $\sim 5$ , respectively). The photocatalytic decolorization of the MeO dye can be described by the first order kinetic model,  $\ln(c_0/c) = kt$ , where  $c_0$  is the initial concentration and  $c$  is the concentration at time  $t$  [4]. Uncertainties in determining rate constants were  $\sim 10\%$ .

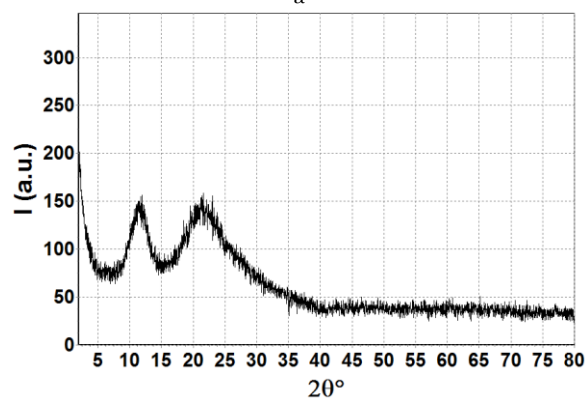
### 3. RESULTS AND DISCUSSION

Comparison of X-ray diffraction patterns of the products of annealing shows that the crystal structure of the initial reagent destroys at  $250^\circ\text{C}$  for  $\text{H}_2\text{O}_2$ -treated (Fig.2) and at  $550^\circ\text{C}$  for untreated (Fig.3) titanil sulfate. The intensity of the peak at  $2\theta \sim 11^\circ$  is higher for TSP250 than for TS550. According to [5], this peak belongs to hydrous titanium dioxide of the general formula:  $\text{TiO}_{2-x}(\text{OH})_{2x}y\text{H}_2\text{O}$ , where  $y$  is about 1.

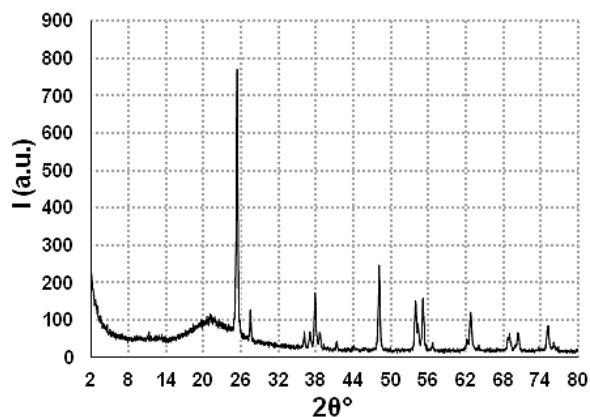
We failed to obtain an XRD for TSP550, since it is hygroscopic.



a

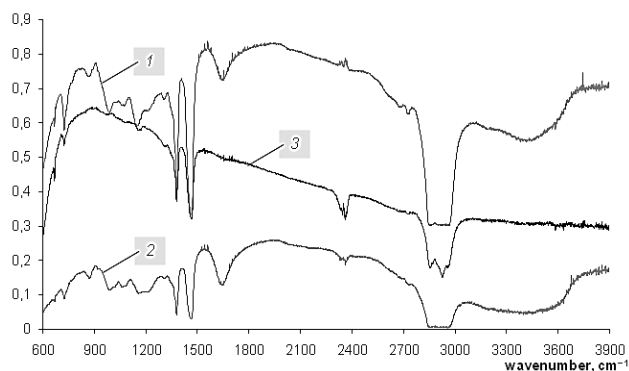


b



c

Fig. 3 – XRD patterns for TS250 (a), TS550 (b), and TS800 (c)

Fig. 4 – IR spectra of pure (1) and  $\text{H}_2\text{O}_2$ -treated  $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$  (2) and TSP800 (3); IR spectrum of TS800 is identical to the spectrum of TSP800

Annealing of H<sub>2</sub>O<sub>2</sub>-treated titanyl sulfate at 800°C produces anatase with very small quantity of hydrous titanium dioxide (Fig.2b), whereas the XRD pattern of the product prepared in the same conditions without H<sub>2</sub>O<sub>2</sub> treatment contains peaks of rutile admixture (~9%) (Fig.3c); this fact is in agreement with [3].

Probably, intermediates formed on H<sub>2</sub>O<sub>2</sub> treating of titanyl sulfate promote its decomposition producing anatase, but prevent transformation of anatase to rutile.

The IR spectra of untreated and H<sub>2</sub>O<sub>2</sub>-treated titanyl sulfate (Fig. 4, curves 1 and 2) were recorded at low temperature, since their spectra recorded at room temperature were poorly resolved.

More disordered spectrum of H<sub>2</sub>O<sub>2</sub>-treated titanyl sulfate as compared to initial reagent, along with XRD patterns of TSP250 (Fig.2a) and TS250 (Fig.3a), indicates that H<sub>2</sub>O<sub>2</sub> destroy crystal structure of titanyl sulfate.

The IR spectra of the samples annealed at 800°C (Fig.4, curve 3) contain no bands of sulfate, hydroxyl and peroxy groups indicating the same chemical composition of the TSP800 and TS800 surfaces (pure titania). So, we can compare correctly their photocatalytic activity.

On contact with water, the TS250 sample forms a colloidal solution; its UV/vis spectrum is similar to the spectrum of TiOSO<sub>4</sub> (Fig. 5). This feature is absent for TSP250 containing predominantly hydrous titania (Fig. 2a). It is additional evidence that H<sub>2</sub>O<sub>2</sub> promotes transformation of titanyl sulfate to titania.

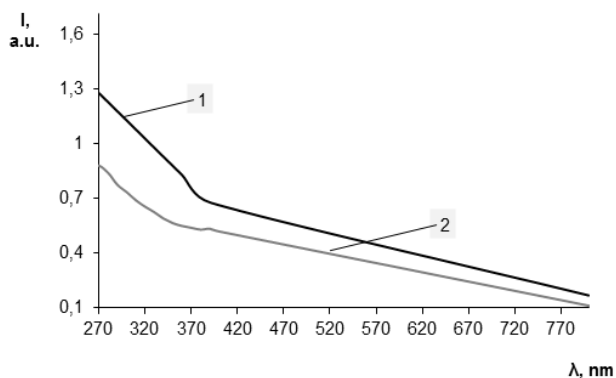


Fig. 5 – UV/vis spectra of the colloidal solutions of TS250 (1) and TiOSO<sub>4</sub> (2).

Higher photocatalytic activity of TS250 as compared to TSP250 (Fig. 6) can be explained by larger contact area of the photocatalyst and substrate. Photocatalytic activity of the samples prepared at 550°C is lower. However, it significantly increases for the samples, annealed at 800°C. This can be caused by sharp decrease of surface protonation, which reflects in the shift of the MeO absorption band (Fig. 6). It is noteworthy, that MeO is an acid–base indicator with the color transfer from red,  $\lambda \sim 505$  nm, to yellow,  $\lambda \sim 470$  nm, at pH 3–4.

Annealing of H<sub>2</sub>O<sub>2</sub>-treated titanyl sulfate at 800°C produces pure nano-crystalline anatase with the highest photocatalytic activity. It is twice higher than for Hombikat UV100, which is manufactured at lower temperature.

Activity of TS800 is lower due to formation of the rutile admixture.

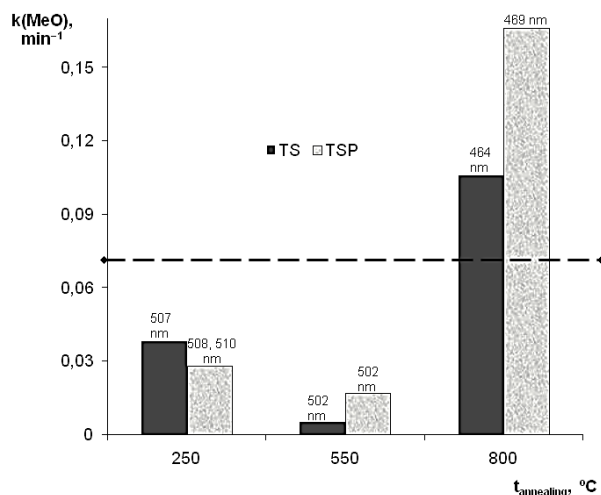


Fig. 6 – Rate constants of the reaction of MeO degradation in the presence of the samples (along with the absorption maximums for MeO) vs. annealing temperature. The horizontal dashed line shows the rate constant for Hombikat UV100 (0.072 min<sup>-1</sup>)

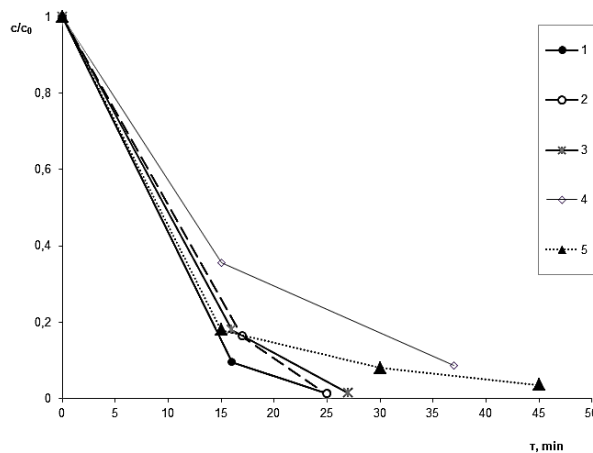


Fig. 7 – Kinetic curves of MeO degradation in the presence of TSP800: 1 – first cycle,  $k = 0.166$  min<sup>-1</sup>,  $\lambda_{\max}(\text{MeO}) = 469$  nm, 2 – second cycle,  $k = 0.072$  min<sup>-1</sup>,  $k = 0.167$  min<sup>-1</sup>,  $\lambda_{\max}(\text{MeO}) = 464$  nm, 3 – third cycle,  $k = 0.152$  min<sup>-1</sup>,  $\lambda_{\max}(\text{MeO}) = 468$  nm, 4 – fourth cycle,  $k = 0.066$  min<sup>-1</sup>,  $\lambda_{\max}(\text{MeO}) = 467$  nm, and at the presence of Hombikat UV100: 5 – first cycle,  $k = 0.072$  min<sup>-1</sup>;  $\lambda_{\max}(\text{MeO}) = 465$  nm

In contrast to most samples of nano-anatase photocatalysts, the TSP800 powder remains white during MeO degradation, indicating facile desorption of the dye. It cannot be explained by low sorption of MeO, since the rate constant of its degradation should be lower in this case. The facile desorption can be caused by the absence of the surface active groups (according to IR spectra, Fig. 4) bonding MeO molecules.

This fact allowed proposing multiple usage of the TSP800 photocatalyst without its washing with water, which is necessary for regeneration of most photocatalysts. Figure 7 shows that photocatalytic activity of the samples decreases noticeably only at the fourth cycle. However, it is still comparable to photocatalytic activity of the first-time used Hombikat UV100.

#### 4. CONCLUSION

Treatment of titanyl sulfate with hydrogen peroxide affects its reactivity. Although peroxy groups decompose at the first minutes of annealing, they promote decomposition of titanyl sulfate producing anatase, but prevent its further transformation to rutile (up to 800°C). As a result, we have prepared nano-crystalline anatase with high photocatalytic activity, exceeding that for the product of annealing titanyl sulfate at similar conditions

without H<sub>2</sub>O<sub>2</sub>-treatment and commercial Hombikat UV100; it does not decrease on the repeated use without any regeneration.

#### ACKNOWLEDGEMENTS

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