



The Sixth Asian School-Conference on  
Physics and Technology of  
Nanostructured Materials

Vladivostok, Russia, April 25 – 29, 2022

P R O C E E D I N G S

Vladivostok  
Far Eastern Federal University  
2022

# Effect of laser treatment of TiO<sub>2</sub> on optical and photocatalytic properties

Z.P. Fedorovich, O.A. Reutova, E.D. Fakhrutdinova\*, V.A. Svetlichnyi  
Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russia

\*e-mail: [fakfrutdinovaed@gmail.com](mailto:fakfrutdinovaed@gmail.com)

**Abstract.** Nanomaterials based on dark titanium dioxide are of considerable interest as promising photocatalysts. In this work, titanium dioxide initially obtained by pulsed laser ablation (Nd:YAG laser with 1064 nm, 7 ns, 20 Hz) was subjected to additional laser treatment. The thus obtained powder materials were annealed and study of the structure by X-ray diffraction, optical properties by diffuse reflection spectroscopy, and photocatalytic properties in the processes of decomposition of the Rhodamine B dye and evolution of hydrogen from an aqueous methanol solution are presented.

## 1. Introduction

The lack of efficient, stable, cheap and environmentally friendly photocatalysts acting in the visible region of the spectrum is currently the main problem in the field of photocatalysis. Recently, a popular object of study is dark titanium dioxide, which has various structural defects and is active in the visible region of the spectrum [1]. Dark titanium dioxide is obtained by various methods: reduction with hydrogen, argon, high or low pressure nitrogen, electrochemical reduction, solvothermal synthesis etc. [1]. A promising way to obtain titanium dioxide in a highly dispersed and highly defective state is the method of pulsed laser ablation (PLA). Previously, by PLA of a metal target in water, we obtained dark defective titanium dioxide, which has absorption in the entire visible range [2]. Additional opportunities for controlling the defectiveness, size and structure are provided by the use of laser treatment of substances at the stage of synthesis. In this work, we show the effect of laser treatment of a colloidal solution of dark TiO<sub>2</sub> on the structural optical and photocatalytic properties.

## 2. Experiment

The materials were prepared as follows. Firstly, the colloidal solution was obtained by ablation of metallic Ti target in water for 1 h using Nd:YAG laser (1064 nm, 7 ns, 20 Hz). Then, for an hour, the colloidal solution was subjected to additional laser treatment with the same laser parameters. Colloidal solutions were dried in air at 60 °C to up to a powder and annealed at different temperatures. Thus, a series of powder materials was obtained.

The samples were studied by X-ray diffraction (XRD), the Brunauer–Emmett–Teller (BET) to identify the specific surface area, and UV-vis spectroscopy. Photocatalytic activity was studied during the Rhodamine B dye decomposition under the LED irradiation with  $\lambda = 375$  and 410 nm. The materials were tested in the process of hydrogen evolution from the methanol solution under LED irradiation with the same wavelength. Prior to the photocatalytic experiment, a suspension containing 50 mg of catalyst in 100 ml of 20 % methanol solution was purged with an inert gas argon. The amount of generated hydrogen was determined using gas chromatography.

## 3. Results and discussions

The initial powders and the samples annealed at 250 °C are X-ray amorphous. The crystal structure is revealed only

after increasing the calcination temperature to 400 °C, anatase predominates in samples (96 %). An increase in the annealing temperature does not lead to a complete phase transition of anatase to rutile; at 800 °C the anatase content is 45%. The laser treatment causes fragmentation of large particles, which is supported by the BET data: laser irradiation results in an increase of the specific surface area from 227 to 253 m<sup>2</sup>/g. All samples absorb in the visible range; however, as the annealing temperature increases, the absorption intensity decreases, but does not disappear completely. The band gap calculated by the Tauc method is approximately 3.07 eV. A decrease in the value of the band gap is associated with the presence of defects in the band gap and thus affects its value.

The data on photocatalytic activity during the decomposition of the dye Rhodamine B show that the samples exhibit high activity both under irradiation at a wavelength of 375 nm and practically do not lose their activity upon irradiation at a wavelength of 410 nm. Complete decomposition of the dye is achieved in 4-4.5 hours. Also, samples annealed at 400 and 600 °C showed good activity in the process of hydrogen evolution from water-methanol solution.

## 4. Conclusions

Thus, additional laser treatment of titanium colloidal solutions after ablation leads to an increase in the anatase content in the samples up to 96%, which is thermally stable. Laser treatment leads to fragmentation of large particles and an increase in the specific surface area, affects the optical and photocatalytic properties. The samples exhibit good photocatalytic activity in the processes of decomposition of the dye Rhodamine B and hydrogen evolution.

## Acknowledgements

This study has been funded from the Russian Science Foundation; Project No. 19-73-30026.

## References

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