



# Effect of reduction/nitriding on structure and photocatalytic activity of tin dioxide



Bikyashev E.A.

Southern Federal University, Rostov-on-Don, Russia

E-mail: eabikyashev@yandex.ru

## Introduction

SnO<sub>2</sub> dioxide crystallizes in the rutile structure and is a direct-gap n-type semiconductor with a band gap of ~3.6 eV. In combination with high stability, non-toxicity, and low cost, SnO<sub>2</sub> is considered as a promising material for the development of photocatalysts for the degradation of organic pollutants in industrial effluents and closed water bodies mainly under UV irradiation. In this work, we studied the effect of treatment of hydrothermally synthesized tin dioxide in reducing (H<sub>2</sub>, NH<sub>3</sub>) and oxidizing (O<sub>3</sub>) media on its composition, structure, and photocatalytic characteristics with respect to rhodamine B (RhB).

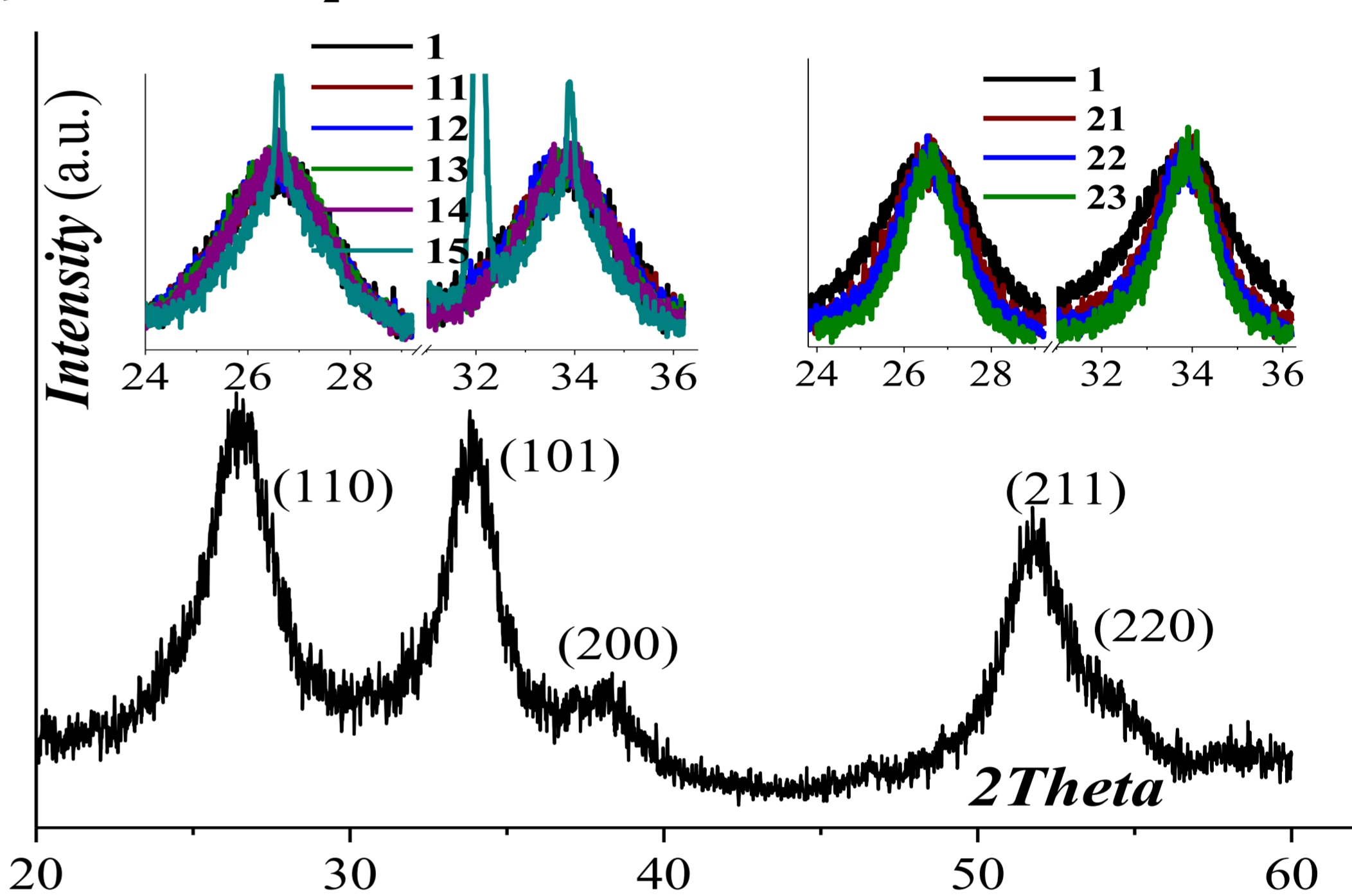
## Synthesis and samples preparation

Hydrothermal synthesis was prepared by dissolving tin metal in cooled nitric acid followed by raising the pH to ~6 with an ammonia solution. An equal volume of isopropanol was added to the final aqueous suspension, after which the reaction mixture was placed in a Teflon reactor and thermally stabilized for 16 hours in a steel autoclave at 180°C. After cooling, the solid phase was washed from nitrates and dried at 60°C.

The resulting weakly crystallized oxide SnO<sub>2</sub> (indicated on the diffraction pattern as sample No. 1) was subjected to 30-minute treatment in a hydrogen flow at 100°C - 150°C - 200°C - 250°C - 300°C (indicated on the diffraction pattern by numbers 11-12 -13-14-15) or ammonia at 300°C - 350°C - 400°C (indicated by numbers 21-22-23). Subsequently, part of the initial SnO<sub>2</sub> phase, as well as samples treated in a reducing atmosphere, were subjected to ozonization (3 hours at 200°C).

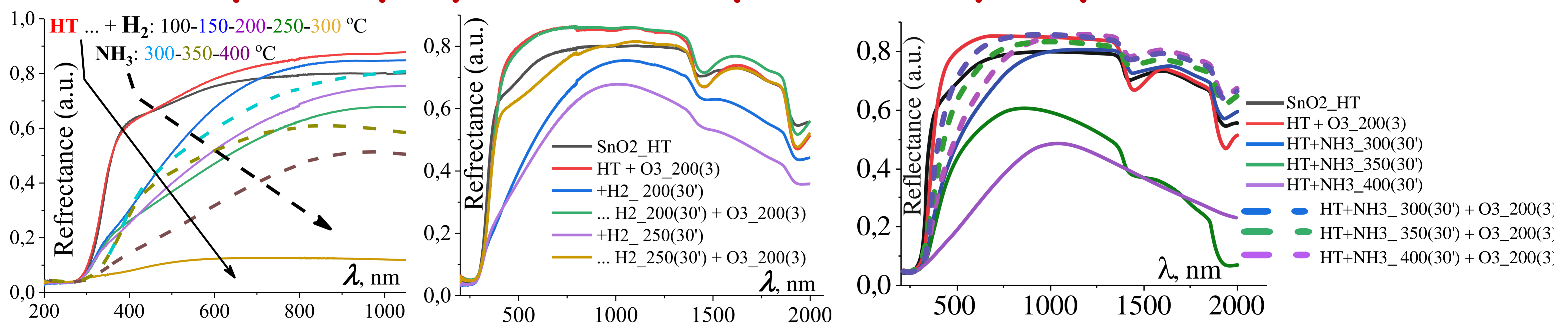
## Characterization

The formation of a weakly crystallized rutile-type phase was established by X-ray diffraction. The average size of coherent scattering regions ( $D_{CSR}$ ) was calculated from the integral width of the reflection (110) using the Scherrer equation. It was ~5 nm. Treatment in H<sub>2</sub>-flow up to 300°C did not affect  $D_{CSR}$ . After holding in a hydrogen flow at 300°C, an impurity of metallic tin was detected (narrow peak on line 15 at  $2\theta = 32$ ). SnO oxide was not detected either by diffraction methods or by Mössbauer spectroscopy. But, simultaneously with the appearance of tin, narrow peaks are observed corresponding to a small fraction of well-crystallized SnO<sub>2</sub>.



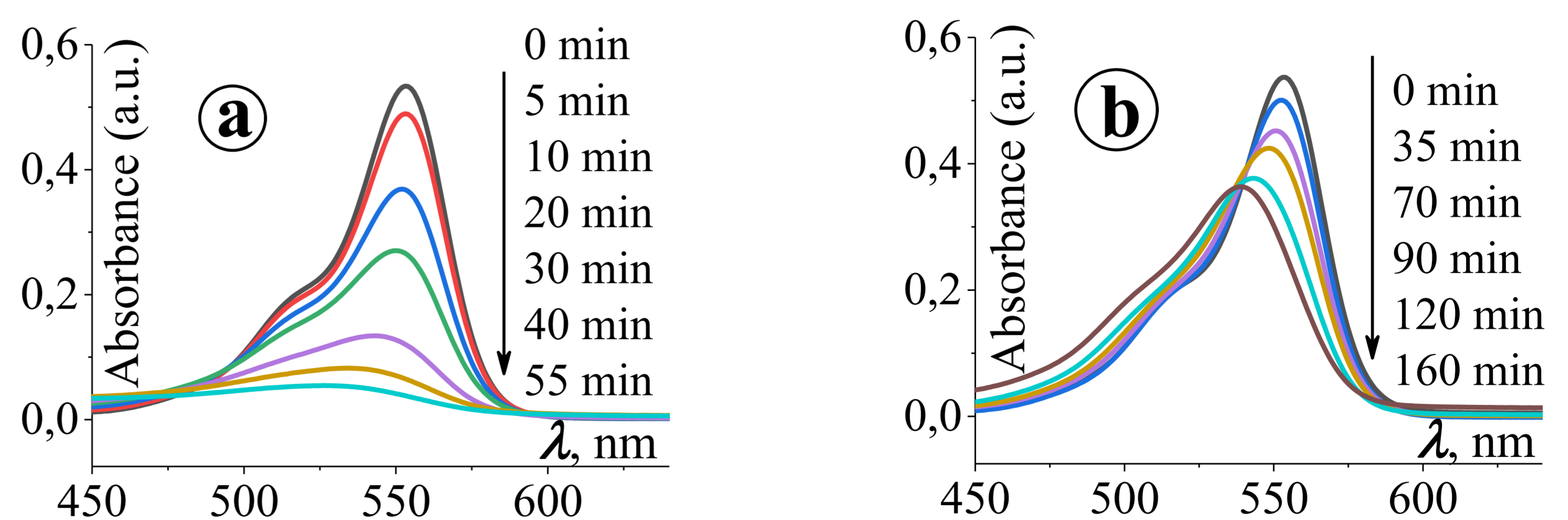
In an NH<sub>3</sub> flow no signs of SnO<sub>2</sub> degradation were found up to 400°C. But the FWHM of the peaks has decreased slightly ( $D_{CSR}$  increased to ~10-12 nm).

## Optical properties and photocatalytic performance



Transformation of the absorption spectral line of RhB in the presence of HT SnO<sub>2</sub> in the UV range (a) and in the visible light (b).

The additionally processed phases are inferior to the original hydrothermal form, possibly due to the rapid recombination of electron-hole pairs. In the future, some of the obtained materials are planned to be additionally composited.



## Conclusions

The influence of reductive (H<sub>2</sub>, NH<sub>3</sub>) and oxidative (O<sub>3</sub>) actions on the hydrothermal phase of SnO<sub>2</sub> has been studied. It has been established that in the H<sub>2</sub> atmosphere already at 300°C, the appearance of metallic tin is observed. In an NH<sub>3</sub> atmosphere, the destruction of SnO<sub>2</sub> does not occur up to 400°C. Ozonation of phases partially reduced by hydrogen makes it relatively easy to reproduce the characteristic absorption corresponding to  $E_g \sim 3.6$  eV. After ozonation of phases reduced with ammonia, the fundamental absorption band of SnO<sub>2</sub> remains shifted to the "blue part of the spectrum". It is possible that this difference is caused by partial nitriding of SnO<sub>2</sub> in an NH<sub>3</sub> atmosphere. The photocatalytic activity of the partially reduced/nitrided SnO<sub>2</sub> phases is inferior to the hydrothermal form of the oxide.