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TITANIUM DIOXIDE NANOTUBES MODIFICATION IN HOT HYDROGEN STEAM

*Dorosheva I.B.[1,2,3], Sushnikova A.A.[3] Valeeva A.A.[1,2], Rempel A.A.[1,3]

1 - Ural Federal University, Yekaterinburg, Russia
2 – Institute of Solid State Chemistry of the UB of the RAS, Yekaterinburg, Russia
3 – Institute of Metallurgy of the UB of the RAS, Yekaterinburg, Russia

*E-mail: i.b.dorosheva@urfu.ru

INTRODUCTION

Nanoscale structures of titanium dioxide (TiO_2) are widely studied for their use in photocatalysis, both for the oxidation of harmful organic substances and for the synthesis of new organic molecules at the visible range of light. At present time, the fabrication of ordered TiO_2 nanotubular structures lays under a great focus of researchers due to their superior performance over TiO_2 nanoparticles. **So, this study is aimed at the synthesis and modification of TiO_2 nanotubes structure and properties for increasing of product yield during organic synthesis in dehydrogenative cross-coupling of (hetero) arenes.**

METHODS

Nanotubes of TiO_2 were synthesized by anodic oxidation of 100 μm thick titanium foil using "Digma" setup with an electrochemical cell, thermostat and power supply. It is carried out at ambient temperature and a 60 V voltage for 60 min in electrolyte of ethylene glycol with fluorine (0.5 wt.% NH_4F). Corrosion-resistant steel was chosen as the cathode material. Subsequent mechanical separation from the titanium foil and annealing was performed to obtain crystalline non-stoichiometric titanium dioxide. The annealing of TiO_2 nanotubes was carried out in a hydrogen flow (from device of the generator of pure hydrogen GPH-12A) within 1 h (in furnace MTF-2MP) at temperatures of 350 °C.

The X-ray diffraction patterns of the synthesized TiO_2 nanotubes before and after annealing in a hydrogen flow were obtained on a STADI (STOE) diffractometer in Cu$K\alpha_1$ radiation with PSD in Bragg-Brentano geometry in stepwise scanning mode with $\Delta(2\theta) = 0.03°$ in the 2θ (10°-80°) angular range. High-resolution scanning electron microscopy ZEISS Ultra 55 microscope was used to study the morphology of the TiO_2. The band gap (E_g) was calculated using the Kubelka-Munk function from the spectra of diffuse optical reflection recorded on an Edinburgh Instruments FS-5 spectrophotometer. The measurement of the specific surface was carried out by the BET method using Gemini VII 2390 analyzer.

RESULTS

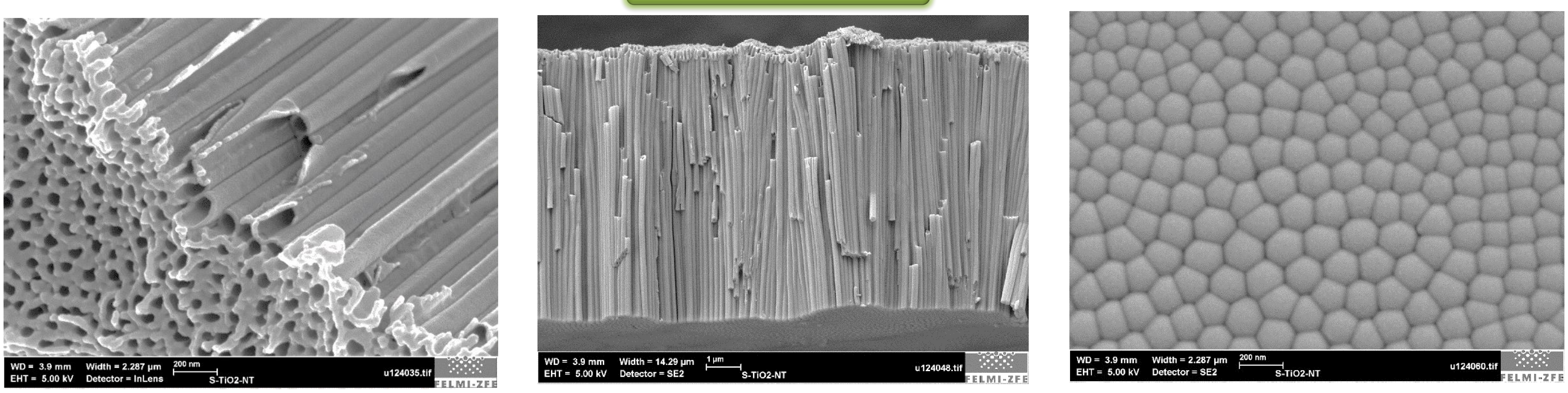

Figure 1 – SEM images of synthesized TiO_2 nanotubes

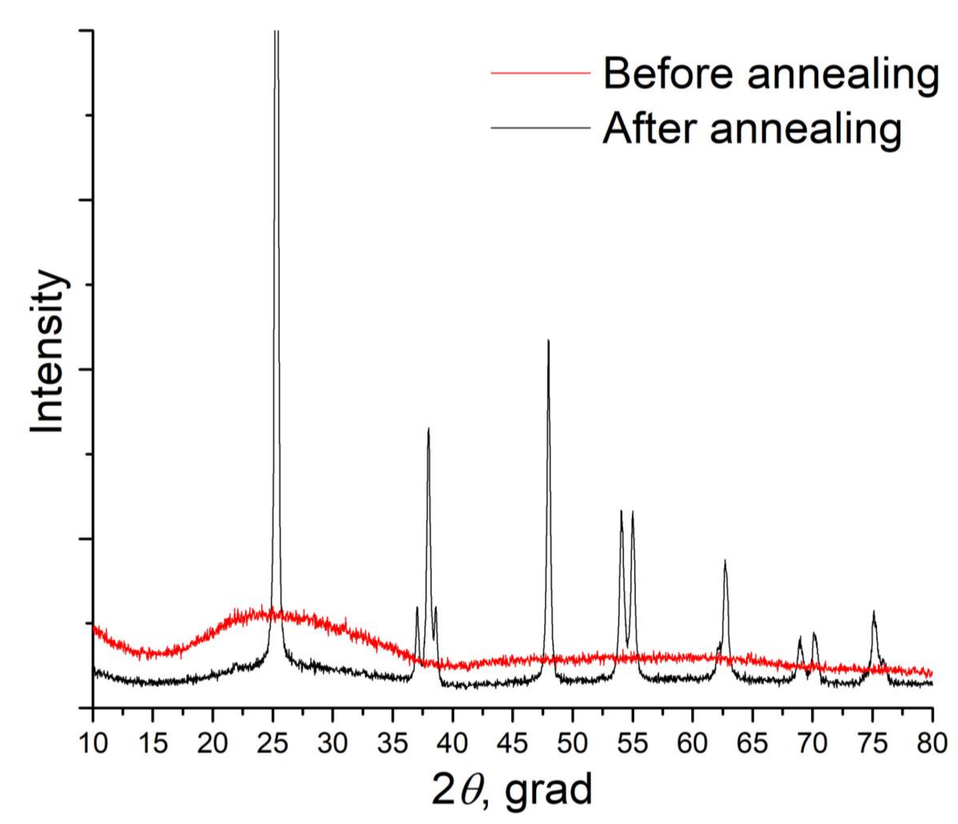

Figure 2 – X-ray diffraction patterns of the TiO_2 before and after annealing

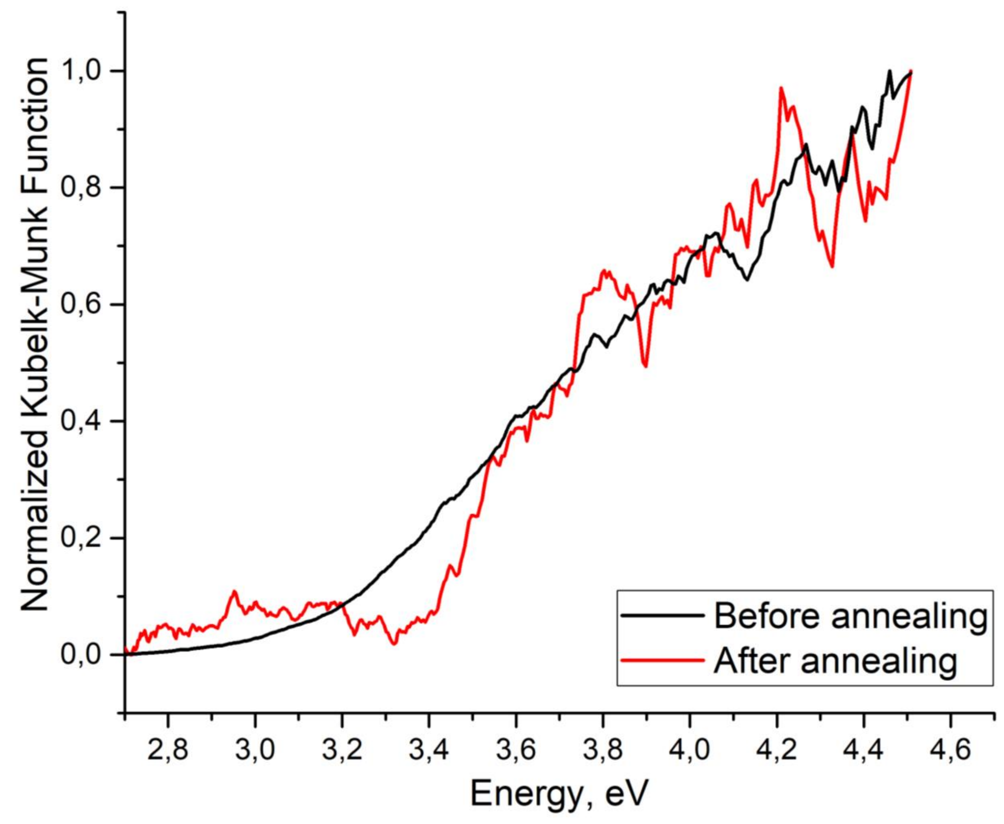

Figure 3 –Diffuse reflectance spectra of the TiO_2 before and after annealing

It was established that synthesized TiO_2 nanotubes have an amorphous structure. The annealing at 350 °C in hydrogen phase transforms from amorphous structure to anatase. The specific surface area and the band gap increases when going from amorphous to anatase phase from 14 to 18 m^2/g and from 3.0 to 3.3 eV, respectively.

CONCLUSION

Proposed in this work anodization conditions allowed to synthesize thick films of titanium dioxide nanotubes which can be were easily separated to use them without titanium foil. According to XRD and BET data, annealing in hydrogen flow at 350 °C and a duration of 1 hour leads to phase transition as well as to an increase in the specific surface area from 14 to 54 m^2/g.

The modified TiO_2 samples will be tested in the oxidative S_N^H cross-coupling of acridine with indole under the same experimental conditions like it was done in [1].

1. Dorosheva I. B., Rempel A. A. et. al., Inorganic materials 55 (1), 21 (2019)

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