# Ion Exchange in Sodium Titanate Nanoribbons and its Application in Dye Photodegradation of Remazol Blue

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Abstract. This work addresses the main point, the synthesis of one-dimensional titanate nanostructures and their ion exchange with transition metals for application in photocatalysis. The catalysts tested in the photocatalytic process were titanate nanoribbons (NRTi) synthesized by hydrothermal method and ion exchanged with  $\text{Sn}^{2+}$ . The structural and morphological analysis of the material was performed by XRD, Raman spectroscopy and TEM images, confirming the formation of the desired structures and the growth of  $\text{SnO}_2$  nanoparticles after the ion exchange process with average size smaller than 10 nm. The values of surface area were obtained by BET and showed a significant increment after the ion exchange process, making it favorable for application in photocatalysis. The NRTi was applied in the degradation of blue dye remazol, generating a total degradation in 120 minutes. The rate constants were calculated from the pseudo-first-order equation.

## Introduction

In the past decade, metal oxides with controlled architectures were shynthesized and they have been the subject of increasing interest due to the novel properties that the nanostructures can provide [1,2]. In particular, titanium oxide nanostructures with good physical and chemical stability are used in different applications such as catalyst supports, supercapacitors [3], humidity sensors [4], rechargeable lithium ion batteries [5,6], photocatalytic cells [7], and dye-sensitized solar cells [2]. Some methods for synthesizing titania or titanate nanostructures with good morphology can be cited, chemical synthesis, electrochemical synthesis and the alkaline hydrothermal method [8].

Since the discovery of a simple route for the synthesis of titanate nanotubes by Kasuga [9], over the last decade alkaline hydrothermal treatment [10-12] has been shown to be an efficient method to produce titanate nanomaterials. This synthesis route can be used to prepare a variety of nanostructures under different hydrothermal conditions, including nanosheets [9], nanotubes [9, 13], nanorods [14], nanowires [15–17] and nanoribbons [11]. Therefore, the development of one-dimensional (1D) photocatalysts with efficient electron-hole formation and favorable recycling characteristics is a challenge for practical applications. 1D titanate structure (nanotubes, nanoribbons, etc) is one of the most important TiO<sub>2</sub>-based materials, because of their large surface areas with advantageous for adsorption of reactive species and reactions dependent of the surface sites [18]. Most of the 1D titanates can only be excited by the UV light, however, the UV light occupies only 4% of the whole sunlight. For an efficient utilization of the sunlight, it is necessary to design the eletronic band structures of the titanates structures to get absorption

of visible light. This band gap engineering has been observed in the titanate nanotubes which were intercalated with Fe and Ag [19,20]

Herein, we show a facile and efficient approach for the preparation of (1D) titanate nanoribbons/Sn/SnO<sub>2</sub> using hydrothermally prepared titanate nanoribbons as a precursor.

## Experimental

The process of synthesis of nanostructured TiO2 nanoribbons (Na-NRTi), based on the alkaline hydrothermal method, included two phases of TiO2, anatase and Degussa P-25. The synthesis was established with a time of 72h and 180 °C. After synthesis the Na-NRTi, the powder obtained was subjected to stirring with SnCl2 in an aqueous medium for 24h at room temperature (RT  $\approx 28$  °C), obtaining Sn-NRTi/SnO2. The crystal structures of samples were analyzed by X-ray diffraction (XRD) collected on a X-ray diffractometer (Shimadzu, Labx-XRD 6000) using Cu-Ka1 radiation. The Raman spectroscopy (Bruker equipment, SENTERRA) was performed using a Olympus BX50 microscope connected to a SENTERRA spectrometer withcharge-coupled device (CCD-"Charge- Coupled Device") and automatic resolution adjustment in 3 cm-1. The excitation light was a 532 nm laser with the output power of 5 mW. The morphologies of the samples were characterized by a FEI Tecnai model G2S - Twin, transmission electron microscopy (TEM) with accelerating voltage of 200 kV. BET specific surface areas were determined by N2 adsorptiondesorption isotherms at liquid nitrogen temperature (77K) using a Quantachrome NOVA 4200 instrument. The samples were degassed at 200 °C in a vacuum for 4h prior to measurement. Photocatalytic potential was done by molecular absorption spectrophotometry in the UV-Vis region, on a Shimadzu UV - 3600 apparatus with scanning in the range between 200 and 800 nm.

### **Results and Discussion**

The morphology evolution of pristine titanate nanoribbons and ion exchanged was observed by transmission electron microscopy (Fig. 1).



Fig. 1. TEM images of the nanoribbons obtained at 180 °C/72h: (a) Na-NRTi/P25; (b) Na-NRTi/anatase and ion-exchanged at RT/24h: (c) Sn-NRTi/P25; (d) Sn-NRTi/anatase

It is observed that the formation of dense titanate nanoribbons with diameters between 20 and 100 nm for samples made using P -25 and up to 200 nm for samples from anatase, and lengths up to several hundred nanometers were observed (Fig 1. a and b). It is possible to observe the coexistence of small particles in the sample of TiO2 - anatase nanoribbons, probably from the precursor used and not totally transformed in those temperature or alkalinity conditions used in the synthesis of these materials.

After 24h of ion exchanged reaction (nanoribbons + SnCl2), it was observed very uniform nanoribbons and the formation of nanoparticles on the surface of nanoribbons. It is possible to see from the Fig. 1 (c and d), the deposition of several particles with average size smaller than 10 nm on the surface of the elongated nanoribbons structures, forming agglomerates which does not permit the definition of the NRTi.

The XRD pattern, Fig. 2 (a and b), of Na-NRTI shows the monoclinic phase as the crystalline sctructure. Furthermore, the characteristic diffraction planes of nanoribbons can be attributed to: around 11° (d = 0,796 nm), assigned to the space between layers; 25°, assigned to the planes formed by the terminal hydrogen bonds; 29°, attributed to the interaction of the terminal bond with sodium and 48°, assigned to the planes formed by the TiO6 octahedral structure. In the Fig. 2 (a and b) is also observed the XRD of nanoribbons after ion exchanged reaction. The peak around 10.2° can be attributed to Na- NRTTi, slightly shifted to 11° of the pristine one. This is an indication that the ion exchange occurred effectively changing the interlayer region. It is also possible to observe a significant difference in the crystallinity of the nanostructures, which decreases upon insertion of the metal Sn2+ (Sn-NRTi).

The XRD pattern of the nanoribbons ion exchanged with Sn2+ indicated that there was a change in the crystalline structure of the NRTi. It is possible to see the formation of very broad peaks indicated in the Fig. 2 which their characteristic have positions of SnO2 nanocrystals. Both precursor phase materials (anatase and P-25) were similarly affected.

To confirm the ion exchange and the XRD characterization, the study was performed by Raman spectroscopy.



Fig, 2. XRD (a and b) and Raman spectra (c and d) of the nanoribbons obtained at 180 °C/72h and after ion-exchanged at RT/24h

Fig. 2 (c and d) depicts the vibrational modes of the Na-NTTi samples before and after ion exchange reactions and indicates changes in the position and intensity of their characteristic bands. The Raman spectrum of the nanoribbons, Fig. 2 (c and d), shows more defined bands around 162 and 195 cm-1, relative to lower energy modes as the Na-O-Ti vibrations. A peak at 162 cm-1 lower and broader to the anatase phase. Also showed bands in the range between 200 and 800 cm-1 relative to the internal Ti-O-Ti vibrations of the octahedra TiO6, characteristic of the Titanate nanoribbons. The mode observed at 923 cm-1 is assigned to Ti-O non-shared vibrations in the Na-NRTI. After the ion exchange, Raman for nanoribbons showed some differences. For both phases (anatase and P-25) there is a slight shift to the lower energy region and a reduction of the intensity of most of its peaks. The characteristic modes have changed after the replacement of Na+ by Sn2+, because of the difference of vibration energy between the bonds. There is an overlap of peaks after the ion exchange observed from modes in the region of 426 and 470 cm-1 which can be attributed to the deformations of internal bonds Ti-O-Ti, forming the crystal lattice and generating a new vibrational mode at 445 cm-1. The mode related to the terminal Ti-O bonds, has a high reduction of its intensity and emerges a new vibrational mode around 828 cm-1, which may be related to the formation of nanoparticles of SnO2 on the nanoribbons surface.

To identify the influence of light on the dye molecules degradation and allow the kinetic study of the synthesized catalysts, we performed a preliminary study of the photolysis (degradation in the absence of the catalyst ) and the catalytic activity of TiO2 precursors that showed a gradual and efficient performance of the degradation of remazol blue (Rb). In particular, the sample of P-25

nanocrystals reduces the concentration of the dy to a minimum after 60 min. Despite presenting a smaller surface area, the sample of P-25 nanocrystals showed to be a better catalyst than anatase nanocrystals, which takes about 120 min to degrade Rb. The reduction of the absorption bands was accompanied by the displacement of peak, which suggests the formation of other organic compounds and therefore not complete mineralization of the dye.

The photocatalytic tests were also carried out with pure nanoribbons and ion exchanged NRTi, which showed a similar profile degradation. From the Figs. 3 and 4 it can be seen that the photocatalytic activity of nanoribbons after 2h of reaction did not achieve the expected results of the advanced oxidation process. These results can be justified by the size of the particles involved and the surface area of the NRTi.

Furthermore, the BET method indicate a significant increment of the surface area of nanoribbons (Na-NRTi/anatase = 34 m2 g-1; Sn-NRTi/anatase = 111 m2 g-1; Na-NRTi/P-25 = 36 m2 g-1 and Sn-NRTi/P-25 = 171 m2 g-1) after the ion exchange reacton. It was observed that the photocatalytic process is not accelerated and the dye takes a long time to degrade. The influence of the elongated structures (NRTi) in the dye degradation is bigger than the surface particles.

From the data obtained, it is observed that, in general, the NRTi/P-25 showed a rate constant greater than those exhibited by the nanostructures of anatase (Fig. 3). This can be justified by its structure, pore size (Na-NRTi/P-25 = 27 nm, Sn-NRTi/P-25 = 3.4 nm, Na-NRTi/anatase = 3.4 nm and Sn-NRTi/anatase = 3.4 nm) and surface area.



Fig. 3. Degradation efficiency of Rb using Na-NRTi.

The low rate of degradation showed Sn-NRTi (Fig. 4) may be associated with the morphology and crystalline structure, making the recombination of charge carriers and reducing the efficiency of the photocatalysis reaction.



Fig. 4. Degradation efficiency of Rb using Sn-NRTi as catalyst.

#### Conclusion

From the hydrothermal method was possible to obtain efficiently the titanate nanoribbons. The Raman and XRD confirmed the ion exchange process with Sn2+, suggesting the formation of nanoparticles of SnO2 and structural changes in the samples after the Sn2+ insertion. TEM images have confirmed the formation of nanoribbons (Na-NRTi and Sn-NRTi) and the nanoparticles of SnO2. Among the catalysts synthesized and applied in the photodegradation of remazol blue, nanoribbons showed a low photocatalytic potential and a lower rate of degradation than expected, possibly caused by their more crystalline structure that trapped the mobility of exciton pairs, responsible for the process degradation of the dye.

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