

Catalysts of TiO_2 and TiO_2/WO_3 Activated in the UV Region and Used in the Photocatalytic Degradation of Methyl Orange

Luana Góes Soares* and Annelise Kopp Alves

Ceramic Materials Laboratory, Federal University of Rio Grande do Sul Av. Osvaldo Aranha 99, sala 705, Porto Alegre-RS, Brazil

*Corresponding author: Luana Góes Soares, Ceramic Materials Laboratory, Federal University of Rio Grande do Sul Av. Osvaldo Aranha 99, sala 705, Porto Alegre-RS, 90035-190, Brazil, Tel: 51996794648 Email: lugoes.soares@gmail.com

Received Date: June 16, 2023 Accepted Date: July 16, 2023 Published Date: July 18, 2023

Citation: Luana Góes Soares and Annelise Kopp Alves (2023) Catalysts of TiO_2 and TiO_2/WO_3 Activated in the UV Region and Used in the Photocatalytic Degradation of Methyl Orange. J Chem Eng Catal 2: 1-11

Abstract

Heterogeneous photocatalysis is an advanced oxidative process that simulates what happens in nature, producing hydrogen by breaking the water molecule by irradiating a solid semiconductor, usually TiO_2 . The synthesis of bicomponent TiO_2/WO_3 catalysts appears as an option to increase the photoactivity of TiO_2 , since only 3% of sunlight can be captured and generate photosensitivity in this oxide. Within this context, this work aims to prepare thin films of TiO_2 and TiO_2/WO_3 bicomponent by spin-coating to function as semiconductors in heterogeneous photocatalysis. The materials were heat treated at 650 °C, 700 °C, 750 °C and 800 °C and their photoactivity was evaluated. The X-ray diffraction technique (XRD) was used to determine the crystal structure formed and the size of the crystallites and the morphology of the films were analyzed by scanning electron microscopy (SEM). The results showed that the mixture with tungsten added to the photocatalytic capacity of TiO_2 , increased the degradation capacity of the samples, resulting in a greater photocatalytic efficiency. The synchrony between TiO_2 and WO_3 , which occurs because the chemistry and physics of these materials are similar, when photocatalytically activated, favors their performance as a semiconductor, increasing the efficiency of the process. Mainly the TiO_2/WO_3 sample that degraded 97% of the dye in 90 minutes of exposure to UV-A light.

Keywords: Films, Semiconductors, Degradation, Heterogeneous Photocatalysis

Abbreviations: AOP: Advanced Oxidative Processes; MG: Methyl Green; MO: Methyl Orange; SEM: Scanning Electron Microscopy; TEM: Transmission Electron Microscopy; UVA: Ultraviolet A (400-315 nm); UV-vis: Visible Ultraviolet (400-800 nm); XRD: X-ray Diffraction; WHT: Without Heat Treatment

Introduction

Currently, among the various methods available to treat environmental decontamination, the Advanced Oxidative Processes (AOP's) stand out. Its mechanism of action is based on the generation of hydroxyl radicals, highly reactive, and with wide application in the removal of the most diverse types of pollutants. Heterogeneous photocatalysis occurs through the irradiation of ultraviolet, visible or infrared light on a semiconductor, which are capable of generating free radicals, such as hydroxyl. Which will excite the electrons from the valence band (VB) to the conduction band (CB), generating the formation of the electron/hole pair, increasing the catalytic efficiency of the process [1].

The use of metal oxides in the degradation of organic compounds has been driven by the fact that they present a chemical and physical behavior that favors their application in photocatalytic processes. The principle of photocatalysis consists in the activation of a semiconductor when exposed to solar or artificial radiation. Within this context, titanium dioxide (TiO_2) is one of the catalysts generally applied in the degradation of organic compounds, mainly due to its unique physicochemical properties [2].

TiO_2 has three polymorphic forms: anatase, brookite and rutile. Absorbs light when it reaches an energy level greater than the gap, electrons migrate to the conduction band generating positive holes in the valence band. Both anatase and rutile absorb ultraviolet rays. Rutile is able to absorb rays that are slightly closer to the visible region, and it would possibly be more appropriate to use it as a photocatalyst. However, anatase has higher photoactivity. The brookite phase is more complex, as it is formed by 8 TiO_2 units, in addition to being difficult to synthesize [2,3].

The main disadvantage is the fact that the photocatalytic capabilities of TiO_2 are activated only when exposed to UV-A light, due to its high band gap (3.2 eV). Because only 3% of the solar spectrum can be used to activate it. Therefore, the present study is justified by proposing the mixture between TiO_2 and WO_3 , aiming to reduce its band gap, increasing the absorption range of TiO_2 in the visible region, and its photocatalytic activity [2,3].

WO_3 is an n-type semiconductor, which has several polymorphic forms, which are: triclinic, monoclinic, hexagonal, orthorhombic and tetragonal. Regardless of the structure formed, all of them are composed of WO_6 octahedrons, joined by the vertices forming chains in a three-dimensional network. It is among the most studied transition metals today, due to its smaller band gap, between 2.6-2.8 eV, which increases the radiation absorption capacity by this oxide in the visible region [4].

Tungsten can also be found in the form of tungstates. These compounds possess the single WO_4^{2-} tungstate ion. There are several ways to get them, among them; from solutions of WO_3 in aqueous alkali. Some examples of tungstates include: wolframite (a solution of FeWO_4 and MnWO_4), scheelite (CaWO_4), stolzite (PbWO_4), among others [4].

Several methods have been used in the deposition of thin films on ceramic substrates; such as: chemical vapor deposition, magnetron sputtering; dip coating, and spin coating among others. Most of the studies using photocatalysts occur with them in suspension (films) or under total mixing (fibers). Applied under total mixing, it has advantages such as: a greater surface area. However, the fact that it is not possible to recover the photocatalyst increases operating costs, associated with mass loss and catalyst separation, has stimulated the use of immobilized photocatalysts. This enables its recovery and subsequent reuse [4].

This confirms the importance of this study, since in addition to the facts mentioned, it also corroborates with the research the fact that the method of preparing the solutions, which make up the films, is innovative. Furthermore, this research, as an agent of scientific propagation, has the scope to contemplate the theme of natural resources, with regard to the construction of mechanisms for sustainable application. With this picture in mind, it would be possible to consider the application of this research in the treatment of effluents, in view of the results obtained with the photocatalytic tests.

Therefore, this work aims to synthesize, characterize films composed of TiO_2 and TiO_2/WO_3 fibers and analyze the photocatalytic behavior of these samples in the degradation of 125 mL of a 20 ppm solution of methyl orange dye, when irradiated with ultraviolet light (UV-A).

Experimental

Reagents

The TiO_2 and TiO_2/WO_3 fibers were obtained from precursors such as titanium propoxide (Sigma-Aldrich), glacial acetic acid (Neon) and polyvinylpyrrolidone (MW 1,000,000 g/mol, Sigma-Aldrich). Anhydrous ethyl alcohol (Zeppelin) was used as solvent. Tungstic acid (Sigma-Aldrich) and hydrogen peroxide (Dynamic Contemporary Chemistry Reagents and Solutions) were used to obtain the WO_3 composites.

Synthesis of TiO_2 and TiO_2/WO_3 fibers

To obtain fibers through the electrospinning technique, a solution was prepared by mixing 2.5 mL of titanium propoxide (TIP), 2.0 mL of glacial acetic acid and 5 mL of an alcoholic solution containing 10 wt% of polyvinylpyrrolidone (PVP). This solution was kept in a dark, enclosed recipient for 15 minutes to complete the hydrolysis reaction and homogenization. Another solution was prepared to obtain the composite fibers by mixing the same components described above and 0.10 g tungstic acid and 1 mL of hydrogen peroxide. This mixture was magnetic stirred at room temperature for 1 hour.

The electrospinning process was set using one of this solution in a plastic syringe connected to a hypodermic stainless steel needle. The needle was connected to the power supply (13.5 kV) applied at a distance of 12 cm from a cylindrical collector. An infusion pump controlled the flow of precursor solution (1.8 mL/h). The cylindrical collector was covered with aluminum foil to allow the nanofibers were harvested. The fibers were removed from the collector every 30 minutes. The obtained fibers were subjected to heat treatment in an electric furnace (SANCHIS) at temperature of 650 °C, 700 °C, 750 °C and 800 °C for 1 hour using a heating rate of 1.4 °C/h, in order to remove the polymeric material and to form TiO_2 and WO_3 .

Thin film preparation

A mixture containing 8 mL of ethanol, 0.8 mL of acetylacetone (Sigma-Aldrich), 0.1 mL of triton X-100 (Sigma-Aldrich), 0.4 g of polyvinyl butyral (MW 30,000 g/mol) and 0.25 g of the heat-treated fibers was prepared using ultrasound bath to homogenize it for 10 minutes. The same procedure was made using the standard TiO_2 -P25 instead of the synthesized fibers. To

form the thin film, 5 drops of the aforementioned mixture was deposited on a 30 mm x 15 mm glass substrate (XOP glass) previously covered with a thin layer of FTO (Fluorine-Doped Tin Oxide). One side of the glass substrate was fixed on the plate of a spin coater (TC 100) and the process was set to achieve a rotation speed of 800 rpm for 30s.

Characterization

The morphology of the obtained materials was identified by scanning electron microscopy (SEM; JEOL JSM 6060). More specific microstructures were analyzed by transmission electron microscopy (TEM, JEOL JEM 1200 Exll) under a voltage of 40 kV to 120 kV. The X-ray diffraction analysis (XRD) was performed using a PHILIPS, model X'PERT® equipment, with $\text{CuK}\alpha$ radiation, operating at a voltage of 40 kV and current of 40 mA, speed 0.05 °/min with a step of 1 s, from 5 to 75 °. The amount of anatase, rutile, brookite and tungsten present in each sample was determined with the aid of the software X'Pert HighScore®. The dimension of the fibers was measured with the aid of UTHSCSA ImageTool® program. To evaluate the photocatalytic activity of the samples, the films were immobilized in 125 mL of a 20ppm solution of methyl orange dye, with pH=7.

The film containing TiO_2 - P25 (Evonik) was used as a standard photocatalyst in order to compare the photocatalytic efficiency of the samples. The photocatalytic reactor operated under constant agitation and temperature (30°C). Air was bubbled during exposure to UV light. Radiation was provided by 12 UV-A lamps (8 W Sylvania F8T5/BLB-black light). 4 mL samples were collected every 15 min, filtered through a 0.2 µm filter and placed in polymethylmethacrylate (PMMA) cuvettes. After the end of the tests, the samples were analyzed by a UV-Vis spectrophotometer (Agilent, Cary-7000; with UMA accessory).

Results and Discussion

Scanning electron microscopy (SEM) images of the surface of films containing TiO_2 and TiO_2/WO_3 fibers are represented in Figures 1 and 2, respectively. Analyzing these images, it was observed that the fibers are randomly oriented, but the microstructure of the TiO_2 fibers seems to be more elongated and continuous than the TiO_2/WO_3 fibers that have a nanorod structure, with an irregular surface. There is an apparent increase in the diameter of TiO_2/WO_3 fibers when compared to pure TiO_2 fibers, probably attributed to the WO_3 clusters [5,6].

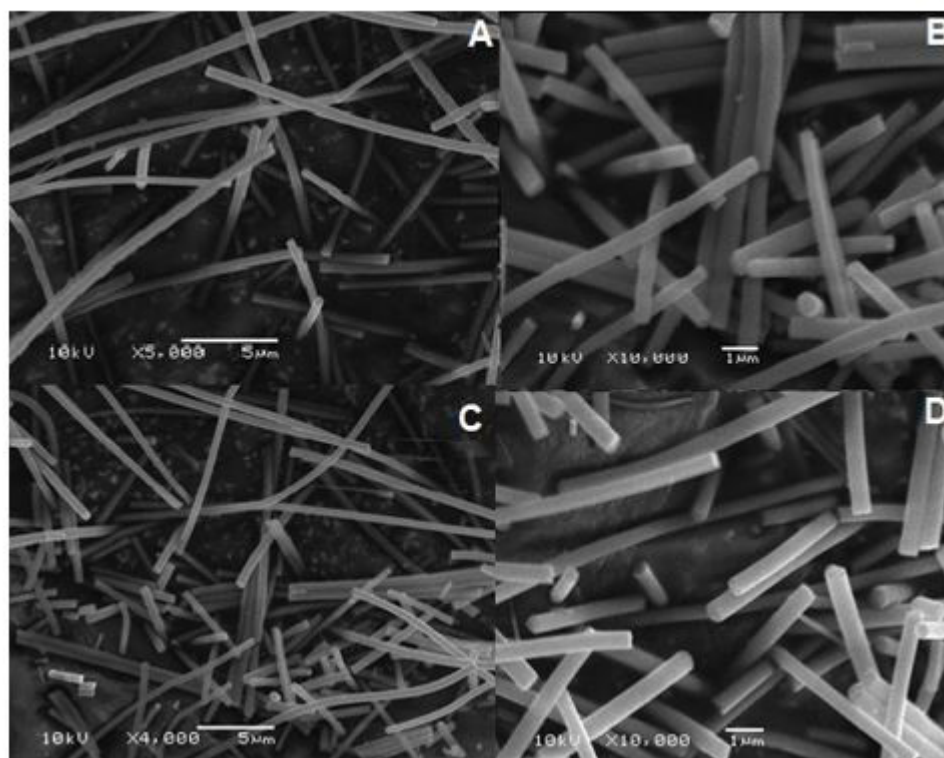


Figure 1: Scanning electron microscopy (SEM) images of TiO_2 films surfaces containing fibers heat-treated at (a) 650 °C, (b) 700 °C (c) 750 °C and (d) 800 °C

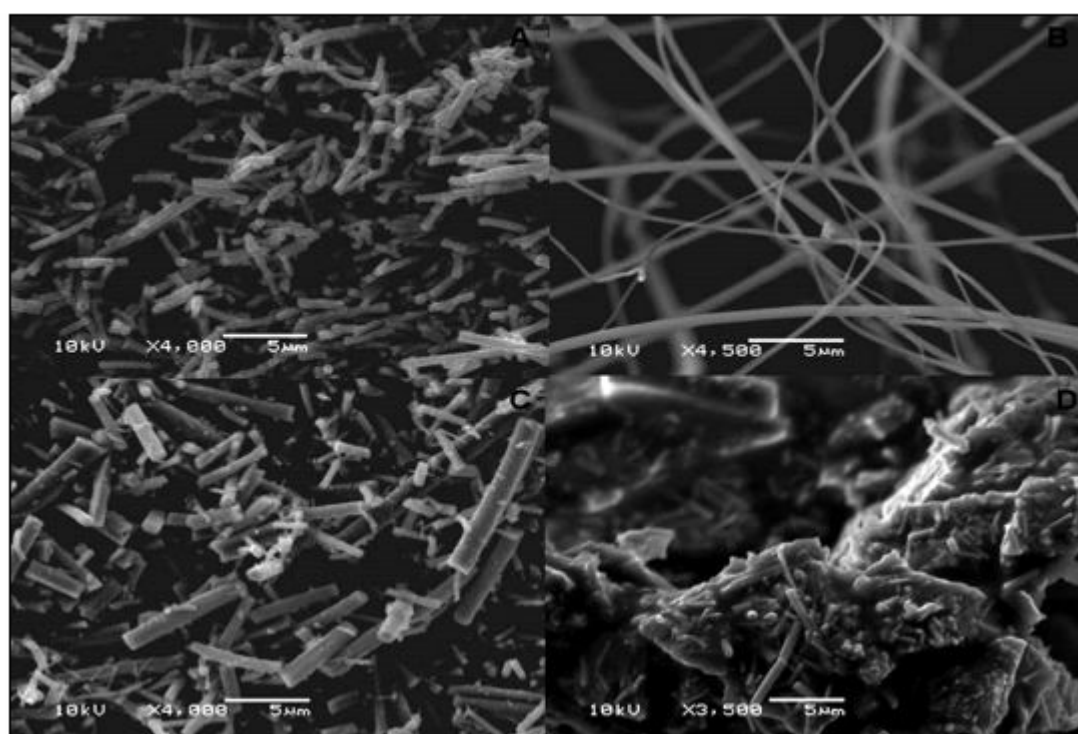


Figure 2: Scanning electron microscopy (SEM) images of TiO_2/WO_3 films surfaces containing fibers heat-treated at (a) 650 °C, (b) 700 °C (c) 750 °C and (d) 800 °C

Figures 3 and 4 show details of the morphological surfaces of the TiO_2 and TiO_2/WO_3 fibers, respectively, observed by transmission electron microscopy (TEM). Figure 3 indicates that the TiO_2 samples present in their composition an agglomerate of

primary particles or interconnected crystals, revealing the presence of grains. Figure 4 is formed by TiO_2/WO_3 samples, where the nanorods, as identified by SEM (Figure 2), also show a larger grain size in their structures [7,8].

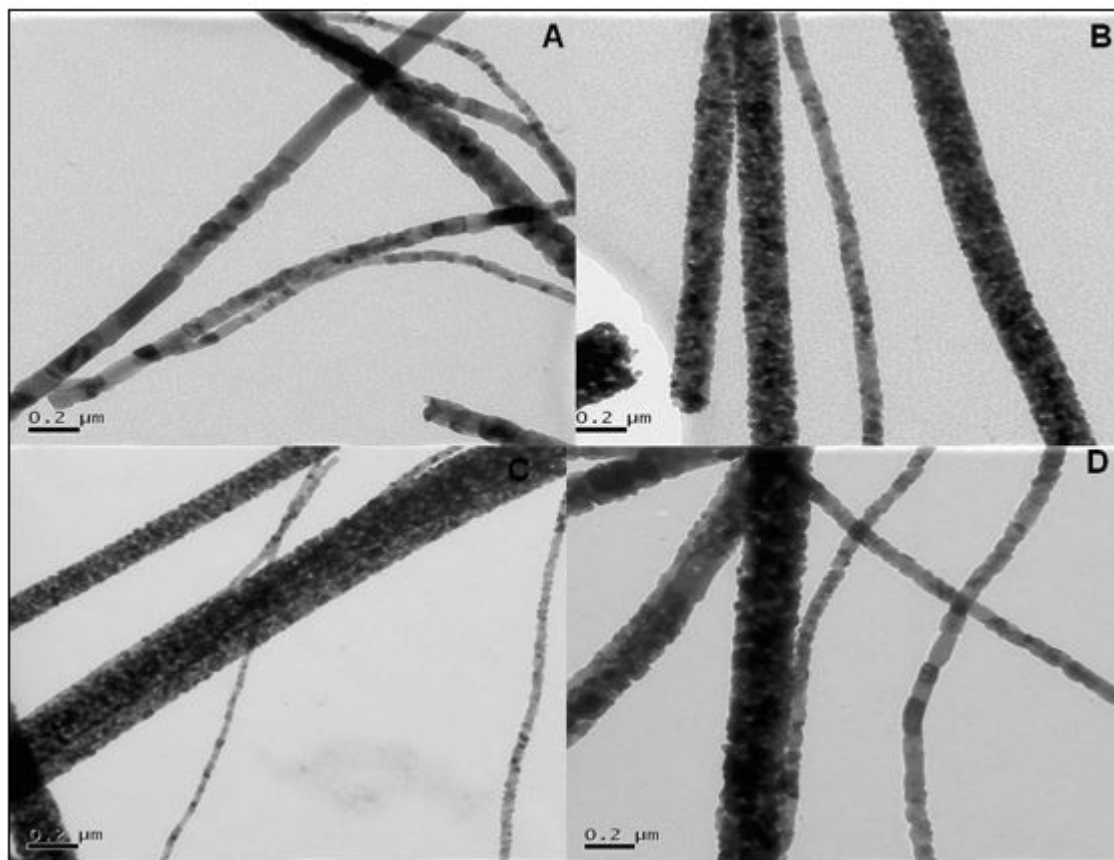


Figure 3: Images for transmission electron microscopy (TEM) of thin films of TiO_2 treated in (a) 650 °C, (b) 700 °C (c) 750 °C and (d) 800 °C

During annealing, the higher the sintering temperature, the smaller the diameter of the nanofibers and the larger the size of the grains that constitute them. This reduction in diameter is due to the removal of the polymer from the surfaces of the

samples. Both TiO_2 and TiO_2/WO_3 films have an axial cluster of many crystals with individual sizes ranging from 24-31 nm for TiO_2 samples and 35-43 nm for TiO_2/WO_3 samples.

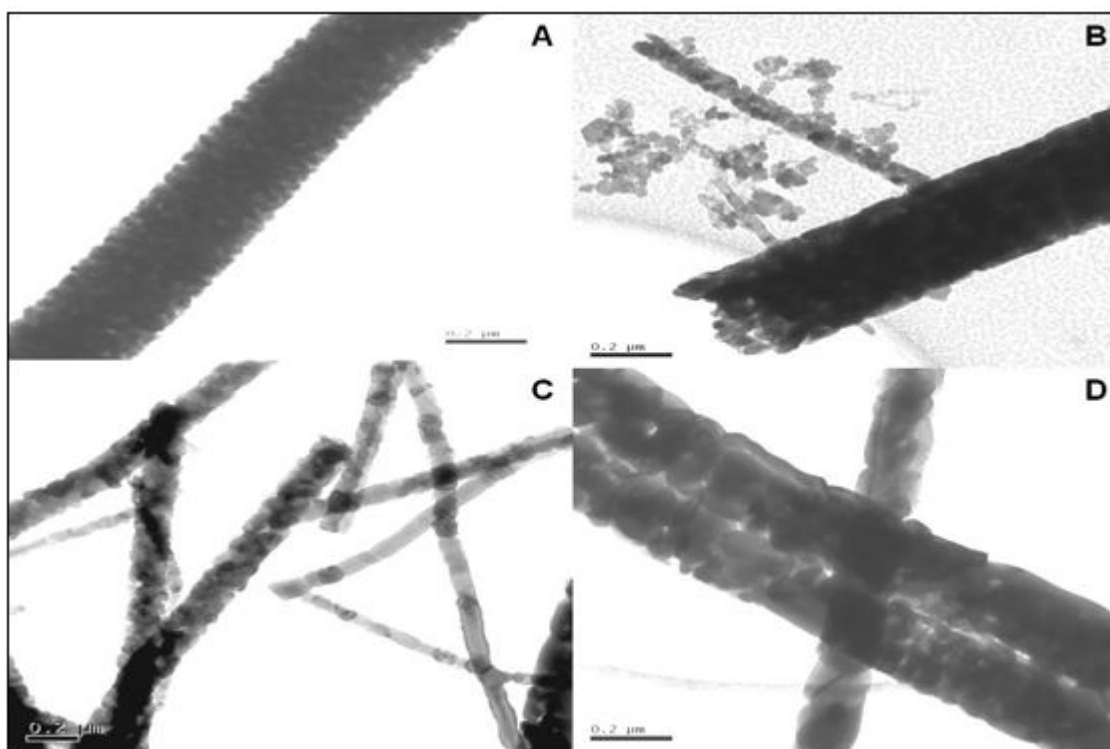


Figure 4: Images for transmission electron microscopy (TEM) of thin films of bicomponent TiO_2/WO_3 calcined at (a) 650 °C, (b) 700 °C (c) 750 °C and (d) 800 °C

The X-ray diffraction (XRD) spectra of the synthesized materials are shown in Figures 6 and 7, respectively. The samples without heat treatment (WHT) were amorphous, that is, before being submitted to the calcination process, the films did not have a defined phase and form (Figure 5). For films containing TiO_2 fibers heat treated up to 700 °C, only the anatase phase was

identified. The rutile phase was identified in the samples treated from 750 °C. The first characteristic peak of the anatase crystalline phase (JCPDS 01-078-2486) appears at $2\theta = 25.271^\circ$. And the first characteristic peak of the rutile phase appears at $2\theta = 27.294^\circ$ (JCPDS 01-077-0442) [2,5,6].

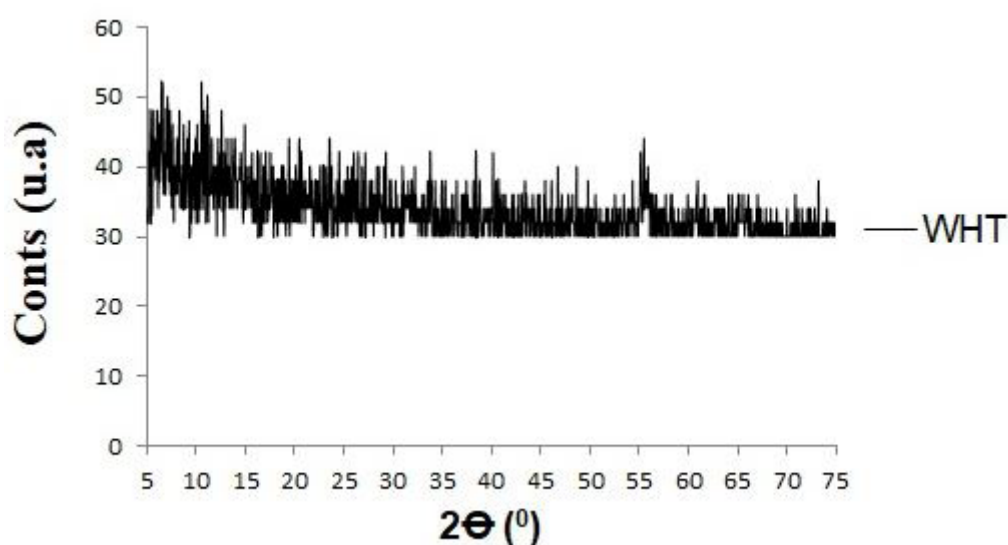


Figure 5: X-ray diffraction spectra of thin films WHT

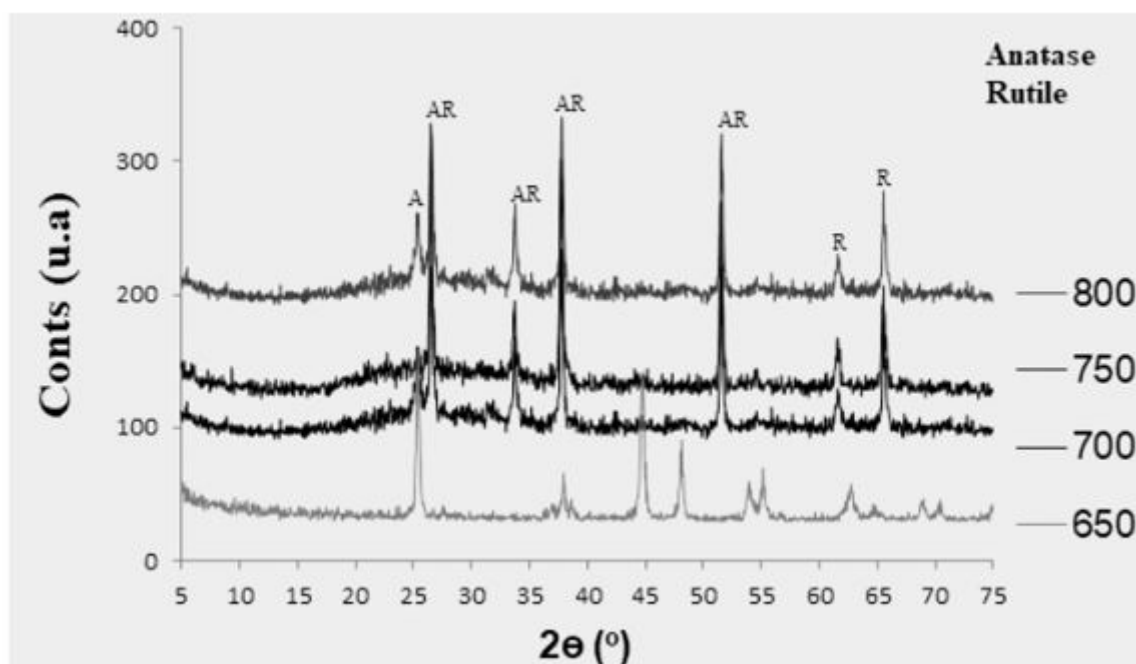


Figure 6: X-ray diffraction spectra of TiO_2 thin films heat treated at 650 °C, 700 °C, 750 °C and 800 °C

As for the films containing TiO_2/WO_3 fibers annealed at 650 °C, the presence of both anatase and brookite was identified. From 700 °C, in addition to anatase and brookite, rutile phases were also identified. The phases identified for WO_3 in the heat-treated samples between 650 °C-700 °C were orthorhombic

(JCPDS 00-032-1393), with a characteristic first peak at approximately $2\theta = 23^\circ$. For the heat treated samples at 750 °C and 800 °C, the tetragonal phase was identified (JCPDS 00-002-0414), with the first characteristic peak at approximately $2\theta = 37.604^\circ$ [3,4].

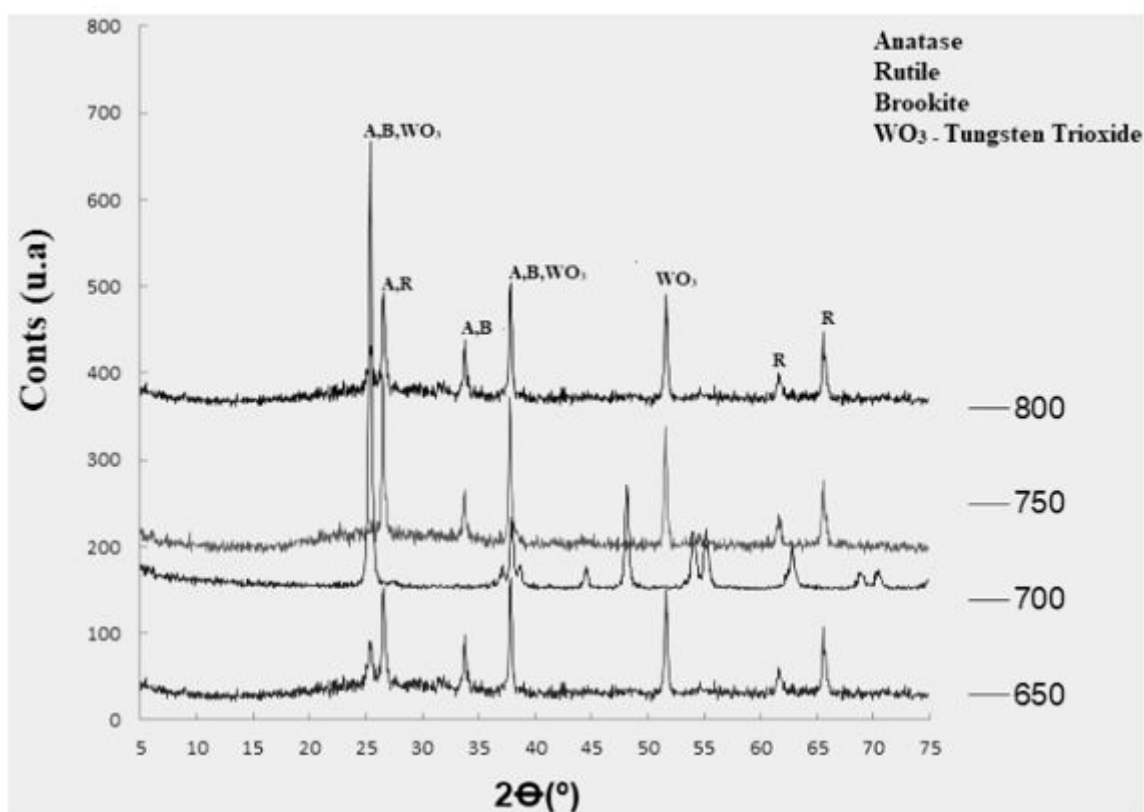


Figure 7: X-ray diffraction spectra of TiO_2/WO_3 thin films heat treated at 650, 700, 750 and 800 °C

Photocatalytic activity

Figures 8 and 9 show the photocatalytic activity of TiO_2 and TiO_2/WO_3 films in the degradation of methyl orange dye during 135 minutes of exposure to UVA light ($\lambda = 365 \text{ nm}$). All samples showed photocatalytic activity. For TiO_2 films, the most photoactive were those that received heat treatment at 650°C , they managed to degrade approximately 25% of the methyl orange dye in 135 minutes of UVA irradiation. The TiO_2 - 800°C films and the P25 standard had a similar behavior, degrading approximately 12% and 14%, respectively, of the dye in 135 minutes of UVA irradiation. TiO_2 - 700°C and 750°C films degraded approximately 19% and 20%, respectively, of the dye in 135 minutes of UVA irradiation. The decrease in degradation effectiveness, observed when the heat treatment temperature increases, is a trend, due to the appearance of the rutile phase, which, in the case of films, is formed from treatments above 700°C . The rutile phase has a lower photocatalytic activity than the anatase phase and, for this reason, its appearance results in a decrease in degradative capacity [2-4].

The presence of tungstic acid (H_2WO_4) in the TiO_2/WO_3 films increased the degradation capacity of these samples. TiO_2/WO_3 films - 650°C , 700°C , 750°C and 800°C degraded approximately 38%, 44%, 60% and 98% of the dye, respectively. It stands out that the $\text{TiO}_2/\text{WO}_3 - 800^\circ\text{C}$ sample was the most effective and fast sample in dye degradation, since in just 90 minutes of exposure to UV-A light it discolored 97% of the dye. This increase in degradation capacity is due to the association between: band gap reduction from 3.05 eV to 2.89 eV, inhibition of electron/hole pair recombination $[(e^-)/(h^+)]$, which allows transfer of loads between TiO_2 and WO_3 , and the increase in the formation of point defects (O_2 vacancies). Charge transfer is fa-

vored by the presence of the hydroxyl group (OH) on the surface of the films, which facilitates the separation of photogenerated electrons/hole. TiO_2 has higher positive potentials than the valence and conduction band of WO_3 . Thus, the conduction band (CB) of WO_3 can act as an electron collector and can pull the CB electrons (e^-) generated in the CB of TiO_2 to its own CB, at the same time, the valence band (VB) of TiO_2 acts like an orifice collector (h^+), therefore, photogenerated orifices are transferred from the VB of WO_3 to the VB of TiO_2 and, therefore, the e^-/h^+ pairs increase the degradation capacity and the efficiency of the process [9,10-11].

The ability of methyl orange (MO) dye molecules to be adsorbed on the photocatalyst surface depends on the concentration of substrates and the formation of hydroxyl radicals. This was also observed by Ejhieh *et al.*, [1], who describes in his work that the discoloration was greater at 40 ppm and then decreased. Because the lifespan of hydroxyl radicals is very short (lasts for only a few nanoseconds) and, therefore, can react only where they are formed. Increasing the amount of dye molecules methyl Green(MG) per unit volume, logically increasing the probability of collision between organic matter and oxidizing species, leading to an increase in degradation efficiency [11].

The concentration of 20 ppm of the dye (MO), used in our photocatalytic tests, contributed to increase the adsorption of the dye at the active sites on the catalyst surface.

The competitive adsorption of O_2 and OH at the sites increased, generating a higher rate of formation of O_2 and OH radicals, which are responsible for the increase in the photocatalytic efficiency of our samples in the degradation of MO [1,11].

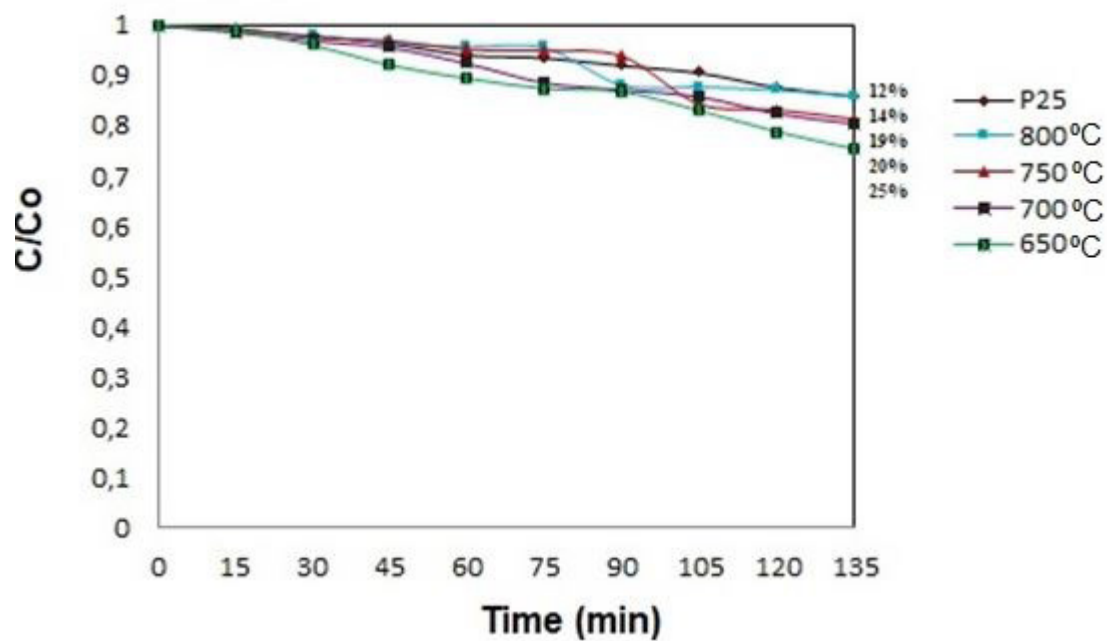


Figure 8: Relative concentration of methyl orange during the photocatalytic test in the presence of TiO_2 thin films and TiO_2 -P25 standard

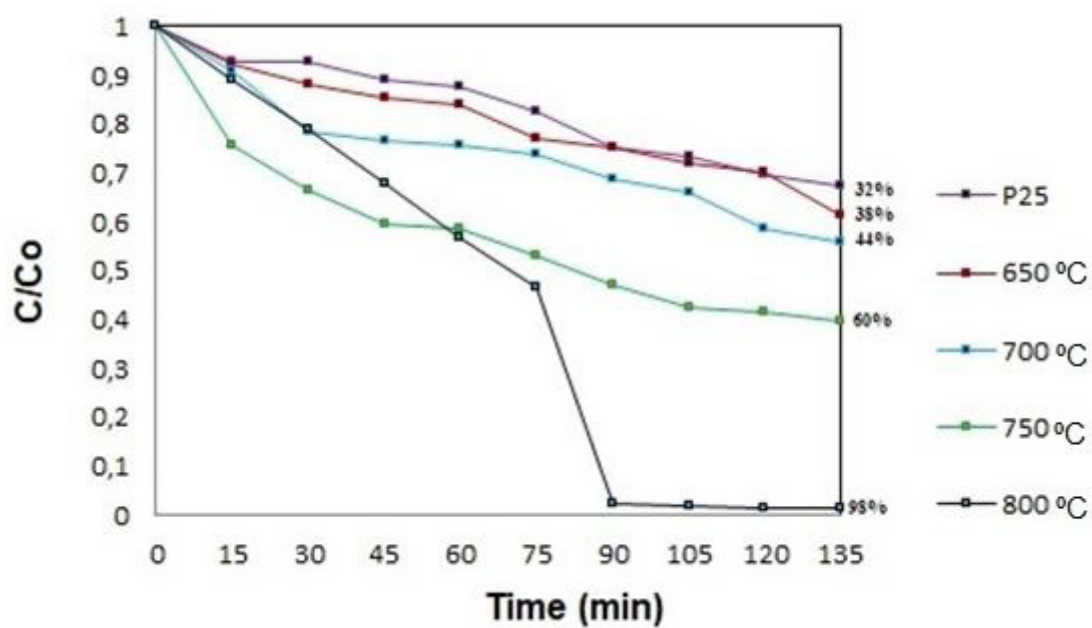


Figure 9: Relative concentration of methyl orange during the photocatalytic test in the presence of TiO_2/WO_3 thin films and TiO_2 -P25 standard

Applications

Heterogeneous photocatalysis can be used for many different purposes. It is a well-established technique, and has been widely used in the degradation of organic contaminants present in wastewater, removal of color in industrial effluents, sewage disinfection, among others. Below we report some recent works, highlighting the variety of applications using heterogeneous photocatalysis, Hunge *et al.*, (2017) [8].

Bharti *et al.*, (2016) [9] produced TiO_2 films doped with different metals, and observed that the best results were obtained with the Fe-doped TiO_2 thin film, due to the increase in the number of O_2 vacancies, associated with the reduction of the gap of the samples. They concluded that the joint action of these two factors produces transparent TiO_2 thin films with good optical properties, making them promising candidates for application as electrodes.

Hunge (2017) [7] reports a promising study for application in water treatment. Where thin layered films of WO_3/TiO_2 were prepared by spray pyrolysis. The best result was achieved using the stratified WO_3/TiO_2 photoelectrode. This sample degraded 66% of the benzoic acid after 320 minutes under sunlight. The result achieved was attributed to the presence of Lewis and Bronsted acid sites (W^{6+} species) that adsorb a greater amount of OH or H_2O , therefore, considered necessary for the generation of OH radicals, and also for mineralization of organic impurities.

Soares *et al.* (2021) [6] describe the use of fibers containing titanium and tungsten oxides for the generation of hydrogen through the water-splitting technique. The most efficient

samples in hydrogen generation were $\text{TiO}_2/\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ - 800 °C fibers. The authors attributed this result to the formation of a greater number of O_2 vacancies [10], due to the increase in temperature, the reduction of band gap. This allowed a greater charge transfer between the two semiconductors, which reduced the chance of recombination of the electron-hole pair, which increased the photocatalytic efficiency in the generation of hydrogen.

Conclusions

All synthesized films were effective in the degradation of methyl orange dye. The presence of tungsten allowed greater stability of the films. This research examined the photocatalytic activity of nanostructures of titanium and tungsten oxides. The results showed that the presence of tungsten precursors favored the photocatalytic properties of the samples, especially the TiO_2/WO_3 - 800 °C films. The high temperature caused an increase in the kinetic energy of the molecules, which reacted quickly, increasing the reaction speed. This generated a large number of vacancies of O_2 and hydroxyl radicals (OH) that quickly adsorbed on the surface of the sample. The association of these factors gave these samples an excellent photocatalytic performance.

Acknowledgment

The authors would like to thank the support provided by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS) and Federal University of Rio Grande do Sul (UFRGS).

References

1. Bahrami M, Ejhieh AN (2014) Effect of supporting and hybridizing of FeO and ZnO semiconductors onto an Iranian clinoptilolite nano-particles and the effect of ZnO/FeO ratio in the solar photodegradation of fish ponds waste water. *Mat Sci Semi Proce* 833-840.
2. Feltrin J, Sartor MNA, De Noni AJ, Bernardin AM, Hotza D, Labrincha JA (2013) Superfícies fotocatalíticas de titânia em substratos cerâmicos. Parte I: Síntese, estrutura e fotoatividade. *Cerâmica* 620-632.
3. Feltrin J, Sartor MN, De Noni AJ, Bernardin AM, Hotza D, Labrincha JA (2014) Superfícies fotocatalíticas de titânia em substratos cerâmicos. Parte II: substratos, processos de deposição e tratamento térmico. *Cerâmica* 19.
4. Silva LGS (2018) Correlação entre as propriedades fotocromicas e atividade fotocatalítica dos óxidos de titânio e tungstênio. Thesis 117p.
5. Soares L and Alves A (2018) Analysis of colorimetry using the CIE-L*a*b* system and the photocatalytic activity of photochromic films. *Materials Research Bulletin* 318-321.
6. Soares LG, Vaz MO, Teixeira SR and Alves AK (2021) Absorbance determination and photocatalytic production of hydrogen using tungsten and TiO₂ oxide nanostructures as catalyst. *Cleaner Eng Tech* 100268.
7. Hunge YM (2017) Sunlight assisted photoelectrocatalytic degradation of benzoic acid using stratified WO₃/TiO₂ thin films. *Ceramics International* 10089-10096.
8. Hunge YM, Mahadik MA, Moholkar AV, Bhosale CH (2017) Photoelectrocatalytic degradation of oxalic acid using WO₃ and stratified WO₃/TiO₂ photocatalysts under sunlight illumination. *Ultrasonics Sonochemistry* 233-242.
9. Bharti B, Kumar S, Lee, Rajesh HNK (2016) Formation of oxygen vacancies and Ti³⁺ state in TiO₂ thin film and enhanced optical properties by air plasma treatment. *Scienti Reports* 1-12.
10. Muccillo ENS (2008) Condutores de íons oxigênio - uma breve revisão. *Cerâmica*, 129-144.
11. Ejhieh AN, Shahriari E (2014) Photocatalytic decolorization of methyl green using Fe(II)-phenanthroline as supported onto zeolite Y. *J Indust Eng Chem* 2719-2726.

Submit your manuscript to a JScholar journal and benefit from:

- ¶ Convenient online submission
- ¶ Rigorous peer review
- ¶ Immediate publication on acceptance
- ¶ Open access: articles freely available online
- ¶ High visibility within the field
- ¶ Retaining the copyright to your article

Submit your manuscript at
<http://www.jscholaronline.org/submit-manuscript.php>