Future Energy
Open Access Journal
ISSN 2832-0328

February 2023| Volume 02 | Issue 01 | Pages 23-26

Journal homepage: https://fupubco.com/fuen

https://doi.org/10.55670/fpll.fuen.2.1.4

Future Publishing LLC

Article

Photodecomposition of water\ethanol mixtures for the production of hydrogen using as catalysts TiO_2 fibers

Luana Góes Soares*[1], Maurício de Oliveira Vaz[2], Sérgio Ribeiro Teixeira[2], Annelise Kopp Alves[1]

[1]Ceramic Materials Laboratory, Federal University of Rio Grande do Sul, Rio Grande do Sul, Brazil
[2]Thin Film and Nanostructure Laboratory, Federal University of Rio Grande do Sul, Rio Grande do Sul, Brazil

ARTICLE INFO

Article history:
Received 02 August 2022
Received in revised form
08 September 2022
Accepted 14 September 2022

Keywords:
Energy, Ethanol, Hydrogen,
Fibers, Water-Splitting

*Corresponding author
Email address:
lugoes.soares@gmail.com

DOI: 10.55670/fpll.fuen.2.1.4

ABSTRACT

The consumption of hydrogen as an automotive fuel has been growing since the 1980s. It can be used both as a gasoline blend and as a pure fuel. All human activities involve the use of energy. Some examples are: fuels for transport and heating, electricity for various purposes, among others. It is a basic element for the production and commercialization of any goods or services and represents one of the main expenses of families. Thus, projected future trajectories for energy prices are of obvious interest to consumers and producers. The use of hydrogen generation and storage technology is an energy generation option to replace current fossil fuels, as it offers the opportunity to obtain energy with reduced environmental impacts and which does not pollute the environment. In this work, TiO_2 fibers were obtained by the electrospinning technique and used as catalysts in the photodecomposition of water-ethanol mixtures for the production of hydrogen. The X-ray diffraction technique (XRD) was used to characterize the synthesized catalysts, the BET method provided measurements of the specific area, and scanning electron microscopy (SEM) analyzed the morphology of the samples. The results indicate that the fibers that contain the anatase phase in greater proportion have a high surface area and were the most effective in the production of hydrogen.

1. Introduction

The increase in energy demand is related to macroeconomic growth, which translates into more disposable income for families, allowing for greater consumption of fuel, electricity, and other energy uses. With this, it is necessary that companies demand more energy, aiming to facilitate a greater production of goods and services. The literature reports that the elasticity/income ratio of energy consumption is around 1, that is, under normal conditions, the percentage increase in an economy causes a corresponding increase in the demand for energy. Countries such as the United States and countries that subsidize fuel, as well as oil-producing countries, which command the rise and taxation of fuel prices, interfere negatively in energy intensity. Currently, energy sources are being sought that combine energy efficiency, energy security, and the reduction of polluting gas emissions into the atmosphere. The generation of energy through H2 creates substantial incentives not only for the adoption of efficiency measures and technologies to reduce consumption but also for the substitution of fossil energy sources. Below we highlight some examples of sustainable energy: plug-in hybrid electric vehicles, ethanol, biodiesel, and hydrogen [1]. Within this context, hydrogen (H_2) has attracted the attention of researchers, due to some characteristics, such as the fact that it can be stored for later consumption, converted into electrical energy, serving as a link between various forms of energy because of its high energy value, among others [2]. Several techniques have been applied for the separation of water, such as catalytic reform of organic compounds and biological processes, aiming at the production of H_2. Using these techniques, hydrogen is obtained by breaking the water molecule [3]. Some ways to produce hydrogen include: primary energy sources (such as coal, natural gas, and oil); intermediate sources (chemicals such as refinery, ammonia, and ethanol), and alternative energy sources (such as biogas, waste gases, and biomass). Obtaining hydrogen using photocatalytic processes is still low. The main disadvantage of using these processes is the possibility of recombination of the electron/hole pair, which is generated during the photocatalytic process. Another factor that contributes to its low use is because TiO_2 has a wide band gap (~3.2 eV), which allows its activation only under UVA light irradiation. Therefore, this work shows the efficient production of hydrogen by water-splitting, using TiO_2 catalysts and ethanol as a sacrificial agent [4].

2. Experimental

For the synthesis of fibers by electrospinning, the following reagents were used: Titanium propoxide (Sigma-Aldrich), glacial acetic acid (Sigma-Aldrich), anhydrous ethyl alcohol (Zeppelin), and a 10% solution by weight of polyvinylpyrrolidone (PVP – Sigma-Aldrich, 1.300,000 g/mol).

3. Methodology

3.1 Obtaining fibers by electrospinning

The first step for the synthesis of fibers by electrospinning was to prepare the precursor solution that contained the mixture of: 2.5 mL of titanium propoxide (TiP); 2 mL of glacial acetic acid and 5 mL of an alcoholic solution containing 10% by weight of polyvinylpyrrolidone (PVP). After completion of the first step, a 5 mL plastic syringe was connected to a 1 mm internal diameter stainless steel hypodermic needle and filled with the precursor solution. The needle was connected to the high voltage source. The distance between the needle tip and a rotating cylindrical collector covered with aluminum foil was 12 cm. A voltage of 13.5 kV was applied between the needle and the collector. An infusion pump (KD Scientific) controlled the flow of the precursor solution (1.8 mL/h). Fibers were collected every 30 minutes for a period of 4 hours daily. After obtaining the fibers by electrospinning, they were subjected to heat treatment in an electric oven (SANCHIS) at temperatures of 650 °C, 700 °C, 750 °C or 800 °C, with parameters of 1 hour and a heating rate of 1.4 °C/min in order to remove polymeric material and form crystalline phases.

3.1.1 Characterization methods

To identify the phases formed in the samples, a PHILIPS X'PERT diffractometer was used, with CuKα radiation, operating with a voltage of 40 kV and a current of 40 mA, a speed of 0.05°/min, and a step of 1 s in the range of 5° to 75°. The diffractograms obtained were compared with the JCPDS database (Joint Committee on Powder Difraction Standards) using the X'Pert HightScore® software. The specific surface area was determined using the Brunauer Emmett Teller (BET) method. The equipment used was an Autosorb Nova 1000e, Quantachrome Instruments. The morphology of the samples was observed through the technique of scanning electron microscopy (SEM). Band gap energy was determined by diffuse reflectance spectroscopy (DRS). The equipment used was a dual-beam UV-Vis-NIR spectrophotometer Cary Agilent 5000, with an integrating sphere in diffuse light reflection mode. The photocatalysis process was carried out in a photocatalytic reactor made of pyrex glass, where the radiation was provided by 12 black light lamps of 8 W each (Fluor BLB T5, Sadokin). After the start of the assay, 4 mL aliquots were withdrawn with a syringe at 15-minute intervals, filtered through a 0.2 µm filter, and transferred to polymethlmethacrylate (PMMA) cuvettes. Then, the aliquots were analyzed for their absorbance Cary 5000, Agilent, with UMA accessory by scanning the wavelength of the radiation λ = 365 nm. The determination of photocatalytic activity was performed based on the C/Co ratio, where C is the molar concentration of the aqueous dye solution with the catalyst at the time of analysis and Co is the initial molar concentration of the aqueous dye solution without the presence of the catalyst.

3.2 Hydrogen production

Hydrogen was produced using a quartz reactor consisting of double walls through which the water circulated, with a constant temperature of 25 0C. After this step, the catalysts, one at a time, were submerged in a solution of 7.5 mL of deionized water and 2.5 mL of ethanol. Before starting irradiation, analytical argon was bubbled through to remove dissolved gases, and the system was deaerated through a vacuum line. To simulate sunlight, a 300 W xenon lamp illuminated the reactor. The gases produced were collected using a Hamilton gas syringe at 30 min intervals for 4 h and quantified using a GC-Agilent 6820 chromatograph. The total volume of samples injected into the chromatograph was 1.000 µL.

4. Results and discussion

Figure 1 depicts the diffractogram of the fibers. The samples without heat treatment (WHT) were amorphous. The TiO_2 catalysts formed anatase (JCPDS 01-078-2486) up to 700 ◦ C. From 750 ºC, rutile (JCPDS 01-077-0442) was also identified. The first characteristic peak of the anatase and rutile phase appears at approximately 2ө = 25.271º e 27.294°, respectively.

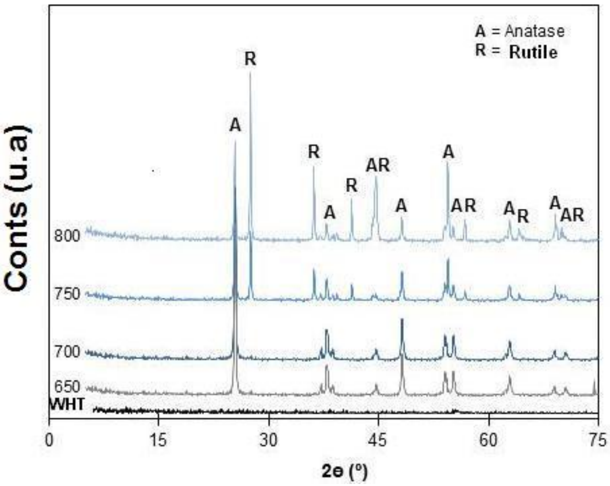

Figure 1. Diffractogram of TiO_2 fibers

Figure 2 shows SEM illustrations of the microstructure of TiO_2 fibers. Analyzing these images, the TiO_2 fibers do not seem to have a preferential orientation, appearing to have an elongated and continuous microstructure.

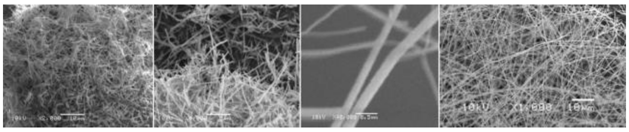

Figure 2. SEM illustrations of the microstructure of TiO_2 fibers

Figure 3 demonstrates the surface area of the TiO_2 fibers. Where it is possible to notice that there is a non-uniform distribution of fiber diameters obtained by electrospinning. This is an undesired characteristic of the fibers formed during the process. Finding a way to control the uniformity of the diameter becomes difficult since the lack of uniformity, apparently, is caused by the inconstancy of the jet during the path to the collector and by the non-uniformity in the division of electrical charges within the fluid.

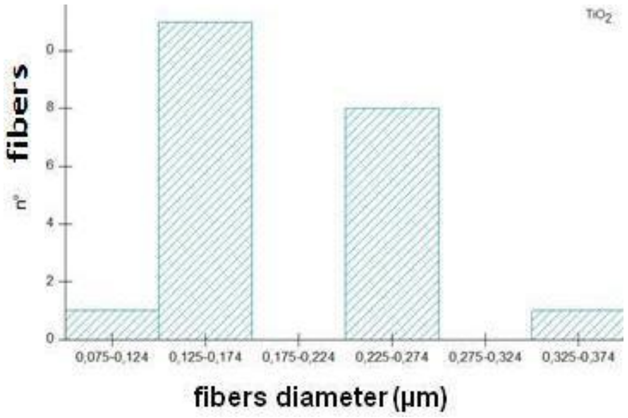

Figure 3. Size distribution of TiO_2 fibers

Table 1 shows the band gap values of TiO_2 fibers synthesized by electrospinning and heat treated at 650 ºC, 700 ºC, 750 ºC, and 800 °C. It is noted that in relation to the TiO_2 P25 catalyst, the values obtained for the synthesized fibers were lower, which indicates that the synthesized materials have a great capacity to act as semiconductors. For all TiO_2 fibers synthesized by electrospinning were able to absorb light in the visible region (400-700 nm) of the electromagnetic spectrum. These differences in band gap values result from the different phases present in the synthesized fibers, from the presence of incomplete bonds on the surface of this material, which influence the reduction of the band gap, which favors the optical properties of the material and also the surface effects on the distribution of electronic levels [2].

By analyzing the results presented in Figure 4, it is clear that the heat treatment temperature benefits the removal of the zone of maximum slope of the absorption curve for longer wavelengths. These changes in the bands correspond to the electron transfer that occurs when the electron passes from VB to CB, where the antibonding 2p orbitals of O_2 (BV) are transferred to the empty 3d orbital of lower energy of Ti^{4+} (BC). The interesting to observe, by comparing the percentages of anatase and rutile with the respective energy gap values described in Table 1 respectively, that the lowest Eg value occurs when the TiO_2 fibers are composed of 100% of the anatase and without the formation of the rutile phase, that is, this is an indication that the reduction in the proportion of anatase in the TiO_2 fibers influences the "gap" value of the TiO_2 band. Band gaps in semiconductor materials are closely related to the absorbed wavelength range, where the gap decreases with increasing absorption wavelength, and which can be proven by the gap values presented for TiO_2 fibers treated thermally at 650 ºC and 700 ºC, which showed a gap of 2.66 eV and 2.90 eV, and absorbed λ= 471 nm and 427 nm, respectively.

Table 1. Band gap and wavelength values corresponding to TiO_2 fibers and P25 standard

Fibers	Samples			
	Band gap (eV)	**λ (nm)**	**Anatase %**	**Rutile %**
TiO_2 P_{25} Evonik	3.20	387.5	80	20
650° C	2.66	471.0	100	-
700° C	2.90	427.0	100	-
750° C	2.94	422.7	50	50
800° C	2.95	420.5	30	70

Figure 5 depicts the catalytic activity of TiO_2 fibers in the degradation of the methyl orange dye during 135 minutes of exposure to UV-A light (λ= 365 nm). The most photoactive TiO_2 samples were those treated at 650 °C and 700 °C, respectively. Due to the majority presence of the anatase phase, proven to be the most photoactive phase of TiO_2 and for presenting the lowest band gap values, 2.66 eV and 2.90 eV, respectively. The presence of anatase in the mixture ensures greater absorption of light. The light absorption of the rutile phase is lower than that of the anatase form, and this lower light absorption results in lower photocatalytic activity. As the heat treatment temperature increases, the formation of the rutile phase occurs, which is the TiO_2 phase with the lowest photocatalytic activity, and its appearance and the increase in the band gap values, 2.94 eV and 2.95 eV, are responsible for the decrease in photocatalytic activity of TiO_2 fibers treated at temperatures of 750 ºC and 800 ºC, respectively.

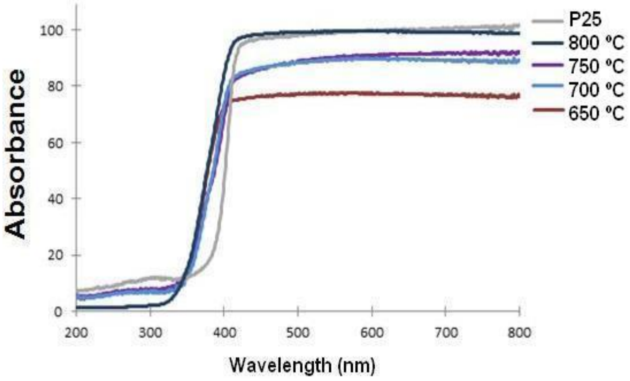

Figure 4. The absorption spectrum of TiO_2 fibers and the P25 standard.

Figure 6 the evolution of H_2 production by the TiO_2–P25 (reference) and TiO_2 fibers. All synthesized samples produced H_2. The highest H_2 production was achieved by the catalysts of TiO_2-650 ºC, with approximately (86.6%) H_2 production capacity. These results confirmed that the heat treatment temperature associated with bandgap mitigation contributed to the formation of a larger number of oxygen vacancies. The conduction occurs through consecutive leaps of O_2 vacancies within the TiO_2 crystal structure in almost all oxygen ion conductors. The joint action of these factors gave titanium structural phase stability. Rising heat treatment temperatures allowed O_2 vacancies to acquire the mobility required to move in a disordered state inside the anionic subnet [5]. In an investigation using ethanol and Pt-doped TiO_2 for H_2 production, it was found that the solution pH impacts the gas production rate. It was indicated that either neutral or basic reaction media H_2 production because OH is absorbed on the catalyst surface, which possibly increases the gas production rate. The OH groups on the catalyst surface might participate in two processes: (1) trapping the holes and (2) transferring charge between the semiconductor and the electrolyte solution. Participation in these two processes mitigates the recombination rates between the electron-hole pairs. Therefore, greater pH in the synthesis of samples could have contributed to enhanced OH groups on the catalyst surface [5].

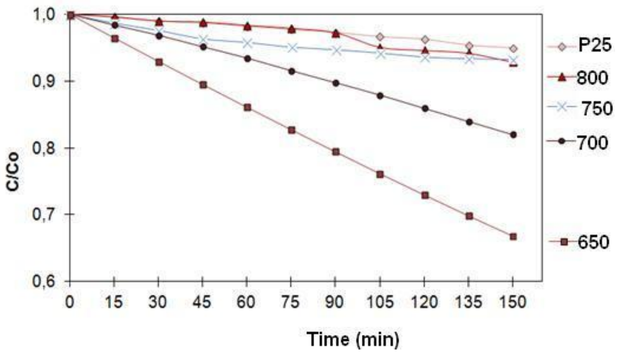

Figure 5. Photocatalytic activity of the fibers and the P25 standard in the degradation of the MO dye

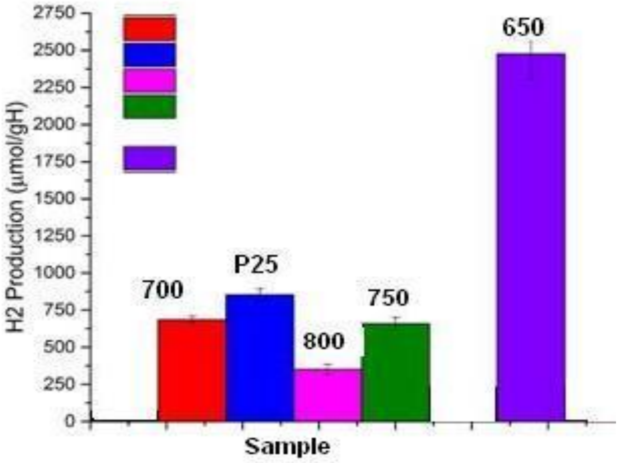

Figure 6. Evolution of hydrogen production using TiO_2 fibers as catalysts and commercial TiO_2 (P25) was presented for comparison

5. Conclusion

With This study showed that the water-splitting technique is a promising route to synthesize TiO_2 catalysts since all synthesized samples demonstrated photocatalytic capacity for the production of H_2, applying ethanol molecules as sacrificial reagents, which functioned as electron donors for H_2 photogeneration in photocatalytic reactions. Among all the synthesized samples, the TiO_2 catalysts heat-treated at 800 ºC had the lowest hydrogen production capacity, probably because TiO_2 in pure water has the highest rate of recombination of the electron/hole pair. The samples heat treated at 650 ºC were the most effective in hydrogen production, reaching 86.6% effectiveness in hydrogen generation. Due to the reduction of sample bandgap, an increase in heat treatment temperature, which increased the concentration of O_2 vacancies (point defects) that played a fundamental role in the movement of the TiO_2 crystal lattice. Which caused a greater photocatalytic capacity and to absorb visible light, which trapped the electrons, thus preventing the recombination of electron/hole pairs.

Acknowledgment

The authors are grateful for the financial support of the Federal University of Rio Grande do Sul (UFRGS), the Coordination for the Improvement of Higher Education Personnel, and CNPq.

Ethical issue

The authors are aware of and comply with best practices in publication ethics, specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. The authors adhere to publication requirements that the submitted work is original and has not been published elsewhere in any language.

Data availability statement

Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

Conflict of interest

The authors declare no potential conflict of interest.

References

[1] E. and Y. Terco, Sustainable Brazil, 2011. https://cuadrivio.net/Publication/vwLUAssets/Sustainable_Brazil_-_World_Cup/_FILE/copa_2014.pdf

[2] L. Silva, Correlação entre as propriedades fotocrômicas e atividade fotocatalítica dos óxidos de titânio e tungstênio, 2018.

[3] L. Soares, M. Vaz, S. Teixeira, A. Alves, Absorbance determination and photocatalytic production of hydrogen using tungsten and TiO2 oxide nanostructures as catalyst, 2021.

[4] C. Rangel, R. Silva, T. Paiva, B. Charrasse, Produção de hidrogénio solar com simultânea mineralização de poluentes orgânicos, 2014.

[5] A. Garcia, W. Guaglianoni, D. Garcia, L. Soares, M. Vaz, S. Teixeira, M. Pereira, T. Basegio, F. Clemens, A. Alves, Fabiano S. Rodembusch, C. Bergmann, Facile synthesis by peroxide method and microwave-assisted hydrothermal treatment of TiO2 with high photocatalytic efficiency for dye degradation and hydrogen production, 2018.