

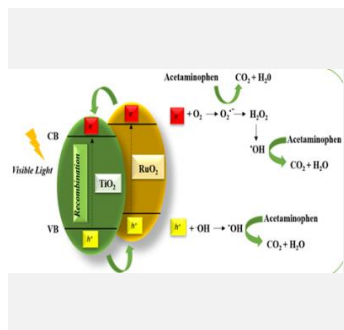
# TiO<sub>2</sub>/RuO<sub>2</sub> mediated visible light photocatalysis for acetaminophen photodegradation: Influence of calcination temperature, ruthenium amounts, and synthesis route on photocatalytic properties

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The photocatalytic degradation of acetaminophen (ACT) has been considered a promising advanced process. To improve the photocatalytic properties of TiO<sub>2</sub>, many strategies have been considered, such as obtaining heterojunctions. For this, TiO<sub>2</sub>/RuO<sub>2</sub> was obtained using three different methods: wet impregnation, co-precipitation, and sol-gel. The structural, electronic, and surface properties were investigated using different characterization techniques, including X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), photoluminescence spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), and N<sub>2</sub> physisorption (B.E.T and B.J.H). After being characterized, all photocatalysts were evaluated for acetaminophen photodegradation.

## Introduction

ACT is one of the most consumed drugs in the world and has been recognized as one of the contaminants of emerging concern due to its persistent and refractory nature. The photocatalytic degradation of ACT has been considered a promising advanced process, as it is a more effective, economical, and easy operation process, with the absence of production of hazardous by-products [1]. Photocatalysis using TiO<sub>2</sub> has become popular and widely studied due to its superior performance compared to conventional methods for the degradation of pollutants in water and effluent treatment. However, the photocatalytic performance of TiO<sub>2</sub> alone cannot meet the needs of commercial applications in the environmental field because of its rapid recombination of photogenerated e<sup>-</sup>/h<sup>+</sup> pairs, in addition to its wide band gap energy (E<sub>g</sub> > 3, 20 eV), which makes it impossible to activate and use it through sunlight and makes it a photocatalyst with low quantum efficiency under certain conditions [2]. To improve the photocatalytic properties of TiO<sub>2</sub>, many strategies have been considered, such as obtaining a *p-n* heterojunction, combining TiO<sub>2</sub> with another *p-type* semiconductor, which is a high-efficiency strategy to build the built-in electric field, which provides impetus to separate e<sup>-</sup>/h<sup>+</sup> pairs photogenerated efficiently, and thus playing an important role in increasing photocatalytic efficiency. In this context, ruthenium oxide (RuO<sub>2</sub>) is a *p-type* semiconductor and is a great representative of the structural modification of TiO<sub>2</sub>, exhibiting band gap energy (E<sub>g</sub>=2,2-2,5 eV) [3]. Recently, RuO<sub>2</sub> has shown excellent combination with TiO<sub>2</sub> in redox reactions such as hydrogen production [3]. Thus, it is observed that the presence of RuO<sub>2</sub> contributes to a synergistic effect for the transfer of photogenerated carriers through the heterostructural interface. In this context, this work aims to obtain TiO<sub>2</sub>/RuO<sub>2</sub>

heterojunctions by different synthesis methods, varying experimental parameters during the synthesis, and later characterize the photocatalysts and apply them in the photodegradation of ACT.

## Material and Methods

### Reagents

Ruthenium(III) chloride hydrate (Sigma-Aldrich), titanium isopropoxide (Sigma-Aldrich), TiO<sub>2</sub>-commercial, polyvinylpyrrolidone (Sigma-Aldrich), Isopropyl Alcohol (Sigma-Aldrich), sodium hydroxide, and nitric acid.

### Synthesis of photocatalysts

The TiO<sub>2</sub>/RuO<sub>2</sub> was obtained using three different methods: wet impregnation, co-precipitation, and sol-gel. For each method, some parameters were selected to be investigated. The different synthesis parameters can control the shape and size of the particle, which are of great interest for the full potential of TiO<sub>2</sub>/RuO<sub>2</sub> to be explored. To understand the properties of heterojunctions, it was essential to characterize them using different techniques to provide answers about structural, superficial, morphological, and electronic information, including, here, investigated by XRD, B.E.T, and B.J.H; DRS; Raman spectroscopy; SEM-EDS.

### Photocatalytic experimental details

ACT was used as a model contaminant to evaluate the photocatalytic activity of the synthesized photocatalysts. Samples were collected over time, filtered, and analyzed by HPLC. An HPLC Shimadzu LC20 chromatograph, equipped with a C18 column (Phenomenex) and with a UV-vis detector (SPD20A) was used to quantify the ACT concentration.

## Results and Discussion

Nanostructured RuO<sub>2</sub> was successfully obtained by the wet impregnation method, with particle size ~23 nm, and for heterojunctions, the proposed method successfully resulted in RuO<sub>2</sub> uniformly distributed on the surface of TiO<sub>2</sub> particles with size ~111 nm. The crystalline structures of the synthesized materials were identified using the XRD technique and are presented in the diffractogram in Fig. 1(a). The results indicate that the heterojunctions between TiO<sub>2</sub>/RuO<sub>2</sub>, in addition to the anatase phase, have the same rutile structure (space group P42/mnm) as TiO<sub>2</sub> and RuO<sub>2</sub> [4]. The optical and electronic properties of the samples were evaluated using DRS UV-Vis, as shown in Fig. 1(b). The introduction of ruthenium resulted in redshift, which can be attributed to the creation of additional energy levels, with the increase in ruthenium content, there was an increase in redshift [4]. To investigate and confirm modification of the crystal lattice in heterojunctions, Raman Spectroscopy analyses were carried out on all materials. Fig. 1(c) shows the results obtained through Photoluminescence Spectroscopy, which were used to investigate the charge transfer behavior of photocatalysts [5].

The photoluminescence spectra indicate broad emissions between 350 and 550 nm, resulting from the different transitions. In Fig. 1 (d), the SEM micrograph clearly shows the nanostructured RuO<sub>2</sub> uniformly distributed over the TiO<sub>2</sub> particles and this trend became more pronounced with the increase in ruthenium content. The photocatalytic activity of individual photocatalysts (TiO<sub>2</sub> and RuO<sub>2</sub>) and heterojunctions with different ruthenium contents obtained by the wet impregnation method was investigated for the photodegradation of ACT under simulated solar irradiation. As shown in Fig. 2, the degradation of ACT obtained with TiO<sub>2</sub> after 120 minutes of reaction was lower than that of RuO<sub>2</sub>, 41.0% and 60.0%, respectively, demonstrating an unsatisfactory result due to its high band gap. For heterojunctions, the efficiency of all was higher compared to individual oxides, and the increase in ruthenium content from 0.5% to 2.5% caused an increase in photocatalytic performance from 84% to 99%, in 30 minutes of reaction. The photodegradation of acetaminophen decreased considerably with increasing ruthenium content, from 99% to 75% for TiO<sub>2</sub>/RuO<sub>2</sub> (2.5%) and TiO<sub>2</sub>/RuO<sub>2</sub> (7.5%), respectively.

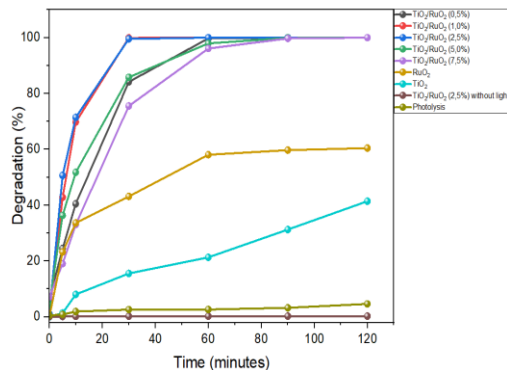
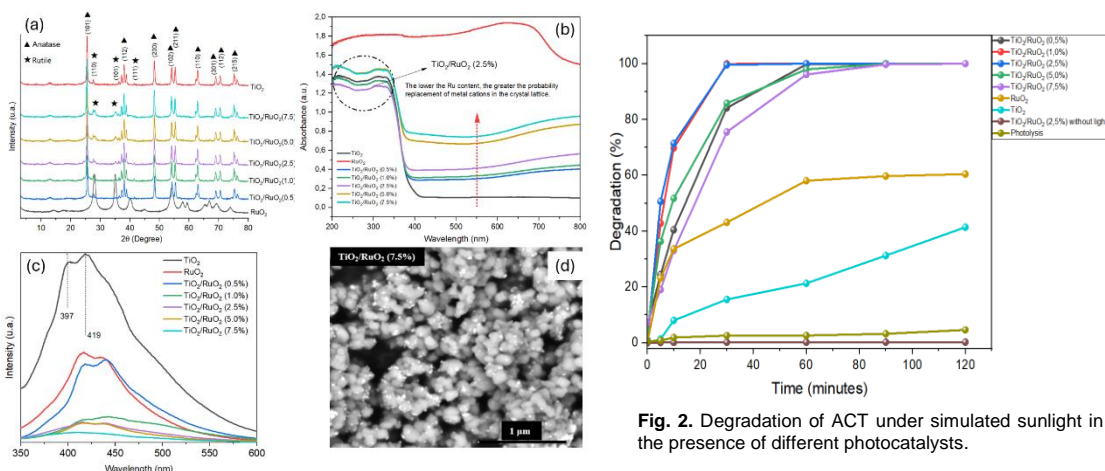


Fig. 2. Degradation of ACT under simulated sunlight in the presence of different photocatalysts.

Fig. 1. (a) XRD; (b) DRS; (c) Photoluminescence Spectroscopy and SEM for TiO<sub>2</sub>, RuO<sub>2</sub> and heterojunctions.

### Conclusions

In 30 minutes of reaction time, an excellent result was possible with the photocatalysts obtained by the wet impregnation method. The synthesis method had a strong influence on the photocatalytic properties of the materials obtained, however, increasing ruthenium content for all methods leads to a decrease in photocatalytic efficiency. Based on the resulting findings to date, the results are encouraging for the efficient degradation of ACT in aqueous media under visible light and mild conditions reactions.

### Acknowledgments

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### References

- [1] J. Lladó, M. Solé-Sardans, C. Lao-Luque, E. Fuente, B. Ruiz. *Process. Saf. Environ. Prot.*, 104 (2016) 294.
- [2] L. Zhang, & M. Jaroniec. *Appl. Surf. Sci.*, 430 (2018) 2.
- [3] J. Tian, X. Hu, N. Wei, Y. Zhou, X. Xu, H. Cui, H. Liu. *Sol. Energy Mater Sol. Cells.*, 151 (2016) 7.
- [4] S. Mihai, D.L. Cursaru, D. Matei. *Sci Rep.* 9 (2019) 18798.
- [5] H. Li, B. Zhu, J. Sun, H. Gong, J. Yu. L. Zhang. *J. Colloid Interface Sci.*, 654 (2024) 1010.