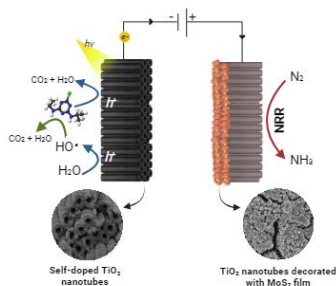


# Contaminant Treatment Simultaneous to NH<sub>3</sub> Production: An Innovative Approach through Photoelectrocatalysis

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Water pollution and CO<sub>2</sub> emissions from the use of fossil fuels have caused alarming impacts on our planet. Due to the dependence of those events, electrochemical processes have emerged as a possibility for treating wastewater through oxidation and, at the same time, generating valuable compounds through reduction reactions. In this context, this work explores the application of photoelectrocatalysis for the mineralization of the herbicide atrazine, simultaneously with the reduction of N<sub>2</sub> to NH<sub>3</sub>. A hybrid reactor was used, where self-doped TiO<sub>2</sub> nanotubes were used for the oxidation of ATZ in the anodic compartment, while a MoS<sub>2</sub> electrode supported on TiO<sub>2</sub> nanotubes surface acted in the reduction of N<sub>2</sub> to NH<sub>3</sub> on the cathodic side. The electrodes were characterized by XRD, SEM-FEG, EDS, ERD UV-Vis, EIS, LSV. The degradation of ATZ and the production of NH<sub>3</sub> were monitored by chromatographic methods. The results show good electrode performance for both reactions, indicating the viability of the method.

## Introduction

Over the years, population growth has been a catalyst for technological progress. However, innovation industrial processes that result in the production of waste and environmental degradation, resulting in undesirable effects on human health and the balance of ecosystems [1], [2], [3].

Among these problems, the growing production of waste is particularly noteworthy. The agricultural sector, for example, is essential to society but generates an extensive volume of contaminants in the environment. Atrazine (ATZ), for example, is a widely used and potentially carcinogenic herbicide that has raised concerns because it is often found in natural waters [2].

The energy sector has also faced sustainability problems since the use of fossil fuels (which emit a lot of CO<sub>2</sub>) accounts for the majority of the world's energy matrix [3]. The environmentally friendly synthesis of NH<sub>3</sub> has been widely explored in this regard. As a sustainable energy vector, NH<sub>3</sub> has been explored as a potential energy carrier, CO<sub>2</sub>-free fuel, and also as a source of electricity and heat. In addition, the production of green NH<sub>3</sub> comes as an alternative to the conventional production process, the Haber-Bosch approach, which has extremely high energy costs [3].

Considering the importance of the efficient treatment of emerging pollutants, as well as the search for substitutes for the fossil fuels currently in use, this study aimed to investigate the use of photoelectrocatalysis for the oxidation of ATZ simultaneously with the production of NH<sub>3</sub>, two processes of socio-environmental relevance.

## Material and Methods

The titanium dioxide nanotubes electrode (TiO<sub>2</sub>Nt) was prepared by electrochemical anodization as

described in the literature [1]. Subsequently, the as-prepared TiO<sub>2</sub>Nt was cathodically polarized at 2.5 V in 0.1 mol KH<sub>2</sub>PO<sub>4</sub> pH 10, obtaining Ti<sup>3+</sup>-TiO<sub>2</sub>Nt electrode [1].

TiO<sub>2</sub>Nt was also used as a platform for the electrodeposition of MoS<sub>2</sub>, generating the TiO<sub>2</sub>Nt-MoS<sub>2</sub> cathode. To do this, a chronoamperometric potential of -1.1 V was applied to TiO<sub>2</sub>Nt in a precursor solution containing 4 mmol L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> and 0.1 mol.L<sup>-1</sup> NaClO<sub>4</sub>, for 1 h [3].

Structural characterization was carried out by X-ray diffractometry (XRD) using a Bruker D2 PHASER diffractometer with Cu K $\alpha$  radiation. High-resolution scanning electron microscopy (SEM-FEG) images were obtained using an FEI Magellan 400 L microscope. Band gap values were obtained by diffuse reflectance using a PerkinElmer Lambda 1050 spectrometer.

The photoelectrochemical activity was assessed by linear sweep voltammetry (LSV), carried out in an Autolab PGSTAT 302N potentiostat at 10 mV.s<sup>-1</sup>, under irradiation from a 300 W Xe source in a 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> electrolyte. Electrochemical impedance spectroscopy (EIS) was obtained in the 10 kHz - 0.03 Hz rms using the same equipment.

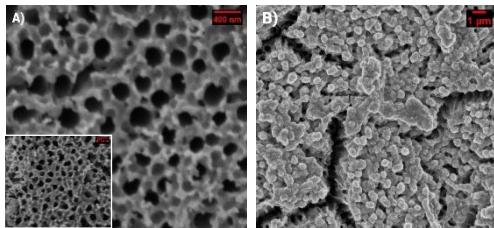
The experiments were conducted at 25°C in a two-compartments cell separated by a PEM membrane. The anode compartment was equipped with the Ti<sup>3+</sup>-TiO<sub>2</sub>Nt photoanode, an Ag/AgCl<sub>(3M)</sub>, and a quartz window. The cathodic side contains TiO<sub>2</sub>Nt-MoS<sub>2</sub> as the cathode electrode, an inlet for N<sub>2</sub> bubbling, and a collecting connection for the NH<sub>3</sub> synthesized.

The electrolyte used on the anode and cathode sides was Na<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup> and Na<sub>2</sub>SO<sub>3</sub> 0.1 mol L<sup>-1</sup>, respectively. Photoelectrocatalysis was carried out in an Autolab PGSTAT 302N potentiostat, applying different potentials under 100 mW cm<sup>-2</sup> of irradiation using a 300 W Xe lamp solar simulator. The amount

of ammonium generated was obtained by the indophenol blue colorimetric method using the Merck Spectroquant® commercial kit [4]. The degradation of ATZ was monitored by HPLC-DAD [4].

## Results and Discussion

Well-aligned and organized arrays of TiONts were obtained through anodization of Ti plates. The FEG-SEM image (Fig. 1A) shows high similarity between the  $\text{Ti}^{3+}$ - $\text{TiO}_2\text{Nt}$  and the  $\text{TiO}_2\text{Nt}$  before polarization (inset of Figure 1A). Figure 1B illustrates the formation of  $\text{MoS}_2$  on the  $\text{TiO}_2\text{Nt}$  surface by the electrodeposition process.



**Figure 1.** FEG-SEM top view images of the electrodes (A)  $\text{Ti}^{3+}$ - $\text{TiO}_2\text{Nt}$  and  $\text{TiO}_2\text{Nt}$  (insert) (B)  $\text{TiO}_2\text{Nt-MoS}_2$ .

LSV results suggest improved photocatalytic efficiency for  $\text{Ti}^{3+}$ - $\text{TiO}_2\text{Nt}$  given a 110% increase in photocurrent compared to pure  $\text{TiO}_2\text{Nt}$  (Figures 2a and 2b), indicating a better PEC efficiency for the first electrode. Nyquist plot (Figure 2c) shows a lower resistance to the charge transfer for  $\text{Ti}^{3+}$ - $\text{TiO}_2\text{Nt}$  comparing to  $\text{TiO}_2\text{Nt}$  indicating a better  $e^-/h^+$  pairs separation and consequently high photocatalytic activity.

The electrocatalytic performance of  $\text{TiO}_2\text{Nt-MoS}_2$  for the reduction of  $\text{N}_2$  to  $\text{NH}_3$  was investigated by LSV under supporting electrolyte saturated by  $\text{N}_2$  and Ar. Figure 2d shows the occurrence of a higher electron transfer to the  $\text{N}_2$  than to the Ar present in the solution

## Conclusions

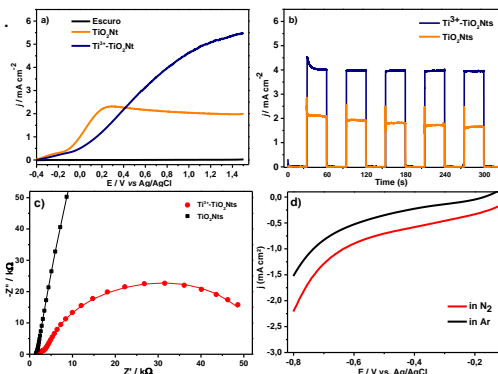
In this work, a photoanode and a cathode based on  $\text{TiO}_2\text{Nt}$  were prepared and used in simultaneous oxidation and reduction reactions. Both proved to be efficient in their specific reactions, demonstrating the possibility of producing a valuable chemical product such as  $\text{NH}_3$  using the same energy that is used to treat waste.

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**Figure 2.** (a) LSV curves (photocurrent) and (b) transient current density (1.0V) in  $0.1 \text{ mol.L}^{-1} \text{ Na}_2\text{SO}_4$  under irradiation from a 300 W Xe source. (c) Nyquist plots at  $5.0 \times 10^{-3} \text{ mol.L}^{-1}$  of the redox pair  $\text{Fe}(\text{CN})_6^{3-/4-}$  (in  $\text{KCl } 0.1 \text{ mol.L}^{-1}$ ) in the range 10 kHz - 0.03 Hz, with a sinusoidal disturbance of 5 mV rms. (d) LSV curve for  $\text{TiO}_2\text{Nt-MoS}_2$  in  $\text{Na}_2\text{SO}_4$   $0.1 \text{ mol L}^{-1}$  saturated with  $\text{N}_2$  and Ar.

The ATZ photoelectrochemical degradation experiments combined with the reduction of  $\text{N}_2$  to  $\text{NH}_3$  were carried out for 2 h. To confirm ATZ degradation and  $\text{NH}_3$  synthesis, the samples were taken from both compartments along the time of reaction.

The photoelectrochemical degradation was performed under different potentials starting from 0.8 V vs Ag/AgCl, where it is observed a most prominent increase in the separation of the  $e^-/h^+$  pairs, generating consequently a higher photocurrent density and a higher possibility for the mineralization of ATZ. The results indicate that ATZ degradation occurred both directly at the photoanode and indirectly via the active intermediate. The protons produced by the oxidation process went across to the cathode compartment through the nafion® membrane, while the electrons were directed to the cathode electrode by the external circuit due to applied potential. In this way, the reduction process was mediated by the electrons generated in the photoanode forming  $\text{N}_2$  radical which reacted with the  $\text{H}^+$  generating  $\text{NH}_3$  in the cathodic compartment.