

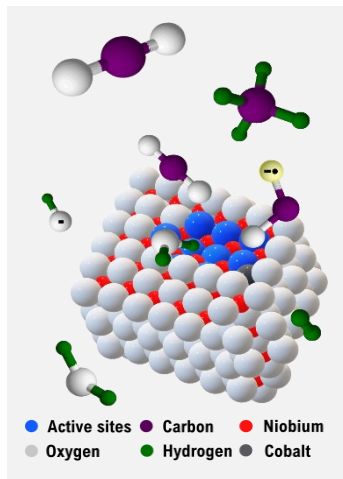
Leveraging Photocatalysis for Renewable Fuel Generation: Advancing Sustainable Energy Production

POSTER

Ph.D. Student: N

Journal: JECE

I. F. B. Silva^{1,2}, V. F. de Almeida², M. G. Rosmaninho³, F. C. C. Moura². (1) Federal Center of Technological Education of Minas Gerais, R. Álvares de Azevedo, 400, Divinópolis, Brazil, izafonte@cefetmg.br. (2) Federal University of Minas Gerais, Av. Antônio Carlos, 6627, Belo Horizonte, Brazil. (3) Federal University of Ouro Preto, R. Diogo de Vasconcelos, 122, Ouro Preto, Brazil.



The widespread use of fossil fuels has led to significant environmental problems. We investigate how reaction time and light sources impact CO₂ and H⁺ photoreduction reactions using niobium(V) oxide-based materials with bandgaps ranging from 1.6 to 3.1 eV. The structure of Nb₂O₅ directly affects the product distribution; synthesised nanosticks produce only CH₄ in 24 h under UVC light, while nanoparticles produce CH₄ in the first hours and H₂ in the finals, as well as methanol and ethanol. The CoNb^(V)O material produces CH₄ in the first 6 hours and H₂ afterwards. Under 465 nm light, it favoured H₂ production. Conversely, Nb^(V)OC_oO only displayed activity under visible light, producing H₂ initially and carbon products after nearly 24 h. The Nb^(V)OMB material favours C-products, particularly under visible light. The absence of CO gas indicates that these photoreactions are effective and environmentally friendly.

Introduction

Using fossil fuels to meet the world's energy and chemical needs has resulted in massive CO₂ emissions, leading to environmental issues like ocean acidification and global warming. Adopting renewable energy sources is crucial to promoting sustainability and tackling the current energy and environmental crisis. Solar fuels, produced with sunlight, offer a promising solution for sustainable energy generation. The production of H₂ from water and C₁/C₁₊ fuel molecules from CO₂ conversion are critical reactions that underpin this approach. This research explores the impact of reaction time and light sources on CO₂ and H⁺ photoreduction reactions using modified niobium(V) oxide-based materials.

Material and Methods

We synthesised the nsNb^(V)O material through a modified hydrothermal route [1]. The synthesis of Nb^(V)O-based materials involved an adapted sol-gel method through the EISA technique [2]. The three chemically modified materials were Nb^(V)OC_oO through wet impregnation of pure Nb^(V)O material, CoNb^(V)O by adding cobalt salt at the beginning of the EISA synthesis, and Nb^(V)OMB through wet impregnation with methylene blue dye. In the photoreactions under UVC light (11 W), we used 300 mg of photocatalyst in 300 mL of deionised water with neutral pH and CO₂ gas saturation. In visible light irradiation source procedures (465 nm, 50 W), we used 10 mg of material in 10 mL of neutral CO₂-saturated water. The photoreactions were carried out for 24 h, and all the products were analysed via gas chromatography with FID and TCD detectors.

Results and Discussion

Understanding the optical absorption phenomenon is paramount for successfully applying amorphous and polycrystalline semiconductors in irradiated systems. In this context, we thoroughly studied the new materials' photophysics properties through diffuse reflectance spectroscopy. Our findings revealed that chemically modified materials presented three absorption states, two within the visible range and the wavelengths varying from 1.6 to 3.1 eV.

The photocatalytic data further revealed that different photocatalysts preferred CO₂ or H⁺ photoreduction, depending on the activation wavelength and reaction time. For instance, under UVC light, CoNb^(V)O produced CH₄ in the first 6 hours of the reaction, followed by the production of H₂ from the 22nd hour onwards, reaching 79.9 μmol g_{cat}⁻¹ in 2 hours. In contrast, it mainly produced H₂ under visible light irradiation in the initial hours (Figure 1). In the liquid fraction, propane-1-ol was identified as the main product.

Transition metal ions have been extensively studied as potential catalysts for facilitating the photocatalytic conversion of CO₂ under suitable energy irradiation [3]. The presence of Co⁺² and Co⁺³ species, along with a high specific surface area (133.5 m² g⁻¹) of this material, promotes a high electron density on the surface during the initial irradiation hours, thereby favouring the 8-electron reaction. The reduction in surface electron density over time, which promotes the 2-electron reaction (HER), may be attributed to the more significant adsorption of CO₂ in the active sites of the material, reducing the charge density on its surface.

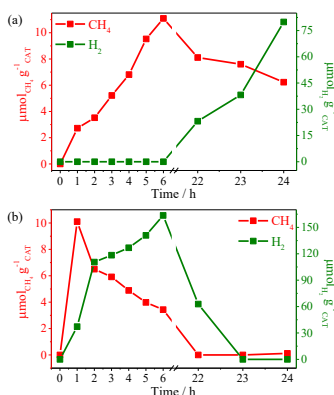


Figure 1. Impact of (a) UVC and (b) visible light irradiation time on gaseous products using CoNb^(V)O photocatalyst.

Furthermore, material Nb^(V)OCoO remained inactive under UVC but displayed CO₂ and H⁺ photoreduction activity under visible light, producing more than 160 μmol g_{cat}⁻¹ of H₂ in the first 22 hours, and after that, it started to catalyse CO₂ photoreduction, producing 12.0 μmol g_{cat}⁻¹ of CH₄ in only 1 hour, in addition to methanol and propane-1-ol. The inactivity observed under UVC irradiation is believed to be due to the fast charge carriers' recombination before they can reach the material's surface. The material's low long-range crystallinity and specific surface area of 50.4 m² g⁻¹ may be mainly responsible for this phenomenon. It is also possible that the generated charge carriers are mainly directed towards internal electron transfer reactions within the material's structure, such as reducing Co⁺³ species.

The crystalline nanosticks material (nsNb^(V)O) displayed remarkable selectivity for CO₂ photoreduction, attributed to its abundant Lewis acid sites that facilitated CO₂ adsorption and subsequent reduction to CH₄. Moreover, its large specific surface area (215.4 m² g⁻¹) and higher crystallinity minimised charge recombination, enhancing the surface's electron density and favouring multi-electron reduction reactions. On the other hand, material Nb^(V)O demonstrated versatility in photoreduction reactions, alternating between CO₂ and H⁺ reduction under UVC irradiation. We observed an initial dominance of CH₄ production within 23 h, followed

Conclusions

The study establishes the critical interplay between the composition and structure of niobium(V) oxide-based materials, the wavelength of irradiation, and reaction kinetics in photocatalytic CO₂ and H⁺ reduction reactions. Under UVC irradiation, the materials had more significant surface charge density and preferred CO₂ photoreduction over hydrogen evolution reaction. However, the reaction pathways can change over time, highlighting the dynamic nature of photocatalytic processes. Ultimately, these findings suggest the potential of photocatalysis as a viable and sustainable energy conversion strategy.

Acknowledgements

The authors would like to acknowledge CNPq, CAPES, FAPEMIG, and INCT-Midas for financial support.

References

- [1] L. Li, *et al.*, J. Mater. Chem. A. 1 (2013) 11894 - 11900.
- [2] P. Yang, *et al.*, Nature. 396 (1998) 152.
- [3] W. Chen, *et al.*, Appl. Catal. B Environ. 244 (2019) 996 - 1003.

by a shift towards H₂ evolution and methanol and ethanol production in the liquid fraction.

These results suggest dynamic surface interactions involving the Lewis and Brønsted acid sites in the nanocrystalline particles and electron transfer kinetics influenced by reaction time. The two behaviours mentioned can be observed in Figure 2.

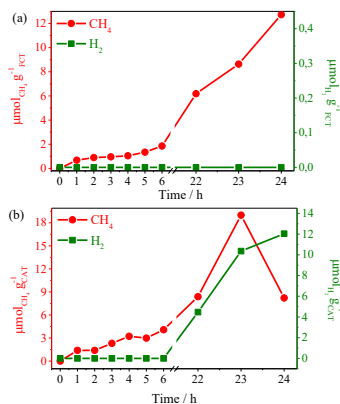


Figure 2. Impact of UVC irradiation time on gaseous products using (a) nsNb^(V)O and (b) Nb^(V)O photocatalysts.

When exposed to UV light, the Nb^(V)OMB material exhibits simultaneous production of CH₄ and H₂. However, it displays selectivity towards methane as the only carbon product. When exposed to visible light, CO₂ photoreduction is the primary reaction, with a significant amount of CH₄, methanol and propane-1-ol produced. Switching the activation light eliminates the competition between photoreductions, although the selectivity of carbon products decreases. The material's performance declines over time due to the leaching of the photosensitising molecule. However, releasing methylene blue molecules into the solution does not pose a disadvantage, as the organic molecule also serves as an electron donor.

It is worth noting that, among the materials tested, all but the photosensitising material demonstrated high efficiency for up to six reaction cycles. These materials only required one washing step between cycles. Notably, no significant amount of CO gas was detected in the photocatalytic reactions.