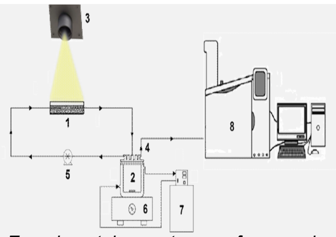
Synergistic Approach for Efficient H_2 Production through Solar Photocatalysis: Cr-doped $SrTiO_3$/ MXene Nanocomposites

Poster
Ph.D. Student: N
Journal: JECE

Héctor Valdés[1]*, *Annamalai Padmanaban[1], and Sivakumar Bharathkumar[1], (1) Clean Technologies Laboratory, Enginnering Faculty, Universidad Católica de la Santísima Concepción, Concepción, Chile. *hvaldes@ucsc.cl*



Experimental set-up for solar photocatalytic water splitting for hydrogen generation: (1) quartz thin-film photocatalytic reactor, (2) stirred jacked tank, (3) solar sun simulator, (4) hydrogen gas outlet, (5) recirculation pump, (6) magnetic stirrer, (7) cooling water bath, (8) gas chromatographer.

Energy demand forecasting is vital for future economic growth and environmental security, guiding energy supply management by both private companies and government agencies. Photocatalytic water-splitting offers significant potential in addressing the global energy and environmental crisis. The challenge lies in developing efficient photocatalysts that meet criteria such as stability, charge separation, and sunlight absorption. While strontium titanate ($SrTiO_3$) shows promise, it suffers from limitations including wide band gap energy, low charge carrier separation efficiency, and rapid recombination. Various strategies, including doping, composites, and heterostructures with other semiconductors, have been applied to improve photocatalytic activity. This study focuses on synthesizing and characterizing chromium-doped $SrTiO_3$/2-D Mxene nanocomposites to enhance charge transportation and reduce electron recombination, aiming for efficient hydrogen production using simulated solar light irradiation.

Introduction

Energy demand forecasting is critical to assuring future economic growth and environmental security. In this regard, photocatalytic water splitting offers enormous promise for resolving the global energy and environmental crisis. The main problem in this technique is to create efficient photocatalysts that meet various requirements, including photochemical stability, good charge separation, and significant sunlight absorption [1,2].

Strontium titanate ($SrTiO_3$) has been used as an effective photocatalyst due to its superior photochemistry, low cost, and ease of manufacturing [3]. However, $SrTiO_3$ has some drawbacks, such as a large band gap energy, limited charge carrier separation efficiency, and rapid recombination, all of which are present in other well-known photocatalysts. All of these disadvantages reduce photocatalytic activity when exposed to sunlight. To address these difficulties, doping, composites, morphological modification, surface treatments, and, in particular, heterostructures with other semiconductors have been designed expressly to boost photocatalytic activity [4].

This study focuses on the synthesis and characterization of chromium-doped $SrTiO_3$/2-D Mxene nanocomposites for H_2 production. The multilayered Mxene and dopant promotes charge transport and reduce electron recombination in the conduction band. The fabrication process was precisely designed to tailor structural and electronic properties, light absorption, and to enhance photo-generated charge carrier separation. The introduction of surface Ti vacancies, as efficient catalytic active sites, accelerates the charge carrier transfer process for efficient H_2 production due to their synergistic effect [5,6].

Material and Methods

The synthesis of Chromium-doped Strontium Titanate (Cr-$SrTiO_3$) incorporated with MXene involved a multistep procedure to achieve proper doping and integration of both materials. Initially, precursor solutions for $SrTiO_3$ synthesis were prepared, with strontium acetate, titanium isopropoxide, and chromium nitrate serving as key components. Simultaneously, MXene was synthesized using a MAX phase precursor, typically Ti_3AlC_2, through selective etching using a solution of hydrofluoric acid (HF). The resulting MXene flakes were washed and collected. Subsequently, the Cr-$SrTiO_3$ nanoparticles and MXene flakes were mixed using ethanol as a solvent, ensuring uniform dispersion via ultrasonication and mechanical stirring. After solvent evaporation, a solid composite material was obtained. This composite underwent controlled calcination that promoted crystallization and optimized integration. Once cooled, the synthesized Cr-$SrTiO_3$/MXene composite was subjected to characterization that included techniques like XRD, UV-Vis, SEM&EDS, XPS to analyze structure, morphology, and elemental composition.

To tune metal-doped $SrTiO_3$ integrated MXene nanocomposites for solar photocatalytic water splitting, 10-50 mg of the photocatalyst were suspended in 100 mL of water with 0.5 M glycerol as a sacrificial agent [7]. Prior to irradiation, dissolved oxygen was purged using N_2 for 20 minutes. H_2 generation was monitored in the dark. Subsequently, the mixture was irradiated for 3 hours using simulated solar light from a solar simulator (sunbrick™), varying lamp-sample distances to assess light intensity effects. Gas chromatography was used to analyze H_2 and O_2 evolution with a thermal conductivity detector using N_2 as a carrier gas. Three cycles of 3 hours each were applied in order to evaluate material stability, with fresh solutions and N_2 purging between cycles. Comparative analysis allowed to monitor H_2 production efficiency under natural sunlight, monitored with a Newport power meter. Triplicate measurements provided average values and standard errors.

The resulting composite material holds promise for various applications, including photocatalysis and energy storage, owing to the synergistic effects between Cr-$SrTiO_3$ nanoparticles and MXene flakes. Precise control over synthesis parameters and adherence to safety protocols were crucial to achieve the proposed goals.

Results and Discussion

Characterization of synthesized materials

The synthesized Cr-$SrTiO_3$/MXene composite was subjected to comprehensive characterization to evaluate its suitability for photocatalytic hydrogen production. X-ray diffraction (XRD) analysis confirmed the presence of crystalline phases, corresponding to $SrTiO_3$, Cr-doped $SrTiO_3$ and Cr-$SrTiO_3$/MXene components and indicating that a successful synthesis and integration of the composite material took place (see Figure 1a).

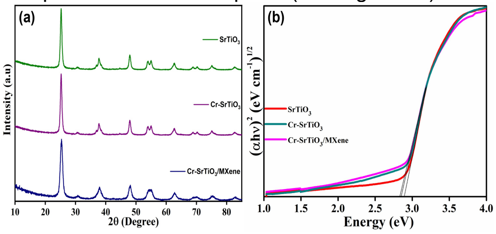


Figure 1. (a) XRD and (b) Tauc plot for prepared materials.

Tauc plots for prepared materials were gathered *via* UV-Vis absorption spectroscopy and results are shown in Figure 1b. From the linear region at higher energies, the interception with the x-axis allows to obtain the values of bandgap energy (E_g) of the synthesized materials. The E_g value offers insights into the material's optical characteristics, crucial for applications like photocatalysis.

Scanning electron microscopy (SEM) images revealed a homogeneous distribution of Cr-doped $SrTiO_3$ nanoparticles on the surface of MXene flakes, facilitating efficient charge transfer and light absorption.

Application for Photocatalytic Hydrogen Production

Photocatalytic hydrogen production experiments were conducted under simulated solar irradiation to assess the performance of the Cr-$SrTiO_3$/MXene composite. Remarkably, the composite exhibited significantly enhanced photocatalytic activity compared to pristine $SrTiO_3$ and MXene counterparts. This enhancement can be attributed to the synergistic effects between Cr-$SrTiO_3$ and MXene, where the presence of Cr dopants facilitates charge separation and promotes surface reactions. In the developed nanocomposite, MXene serves as an excellent electron conductor and provides a large surface area for catalytic reactions.

Moreover, experimental results show that the composite exhibited excellent stability and recyclability over multiple cycles of hydrogen production, highlighting its potential for practical applications.

The Cr-$SrTiO_3$/MXene composite holds great promise for photocatalytic hydrogen production, offering several advantages over traditional photocatalysts. Firstly, the synergistic combination of Cr-$SrTiO_3$ and MXene leads to enhanced photocatalytic activity, enabling efficient utilization of solar energy for hydrogen generation. Secondly, the composite exhibits excellent stability and recyclability, making it suitable for long-term and continuous hydrogen production. Additionally, the abundance and low cost of the precursor materials make the composite economically viable for large-scale production.

The application of the Cr-$SrTiO_3$/MXene composite in photocatalytic hydrogen production has the potential to address the growing demand for clean and renewable energy sources. By harnessing solar energy to drive the conversion of water into hydrogen, this composite offers a sustainable solution to mitigate climate change and reduce dependence on fossil fuels. Furthermore, the versatility of the composite opens up opportunities for integration into various photovoltaic and energy storage systems, paving the way for a greener and more sustainable future.

Conclusions

The synthesized Cr-$SrTiO_3$/MXene composite shows to be an efficient photocatalyst for hydrogen production under simulated solar irradiation. The successful synthesis of the Cr-$SrTiO_3$/MXene composite enhances the photocatalytic activity, offering superior performance compared to individual components with excellent stability and recyclability. This composite holds potential for addressing global energy and environmental challenges, offering a sustainable solution for clean hydrogen generation. Further research should focus on optimization and exploring additional applications, marking a significant step toward realizing renewable energy solutions for a greener future.

Acknowledgments

This work was supported by ANID, FONDECYT/Regular N° 1240705 and by ANID FONDECYT/Postdoctorado N° 3220176 to whom the authors are indebted.

References

[1] Zhao, Z., Zhang, H., & Qu, Z. (2021). Journal of Materials Chemistry A, 9(5), 2463-2498.

[2] Zhang, T., & Wang, P. (2020). Advanced Energy Materials, 10(17), 1903363.

[3] Liu, Y., Jiang, Y., & Zhang, H. (2022). Journal of Materials Chemistry A, 10(4), 1852-1873.

[4] Dong, G., Sun, X., & Ho, W. (2021). Chemical Engineering Journal, 427, 131898.

[5] Zhao, Z., Zhang, H., & Qu, Z. (2020). Advanced Energy Materials, 10(21), 2000186..

[6] Wang, Z., Dong, B., & Liu, X. (2022). Catalysts, 12(1), 14.

[7] Zhu, M., Wang, Y., & Xu, L. (2023). Journal of Materials Chemistry A, 11(10), 4963-4976.