Exsolution in $LaNi_xFe_{1-x}O_3$ Perovskite Films for photocatalytic reform of H_2

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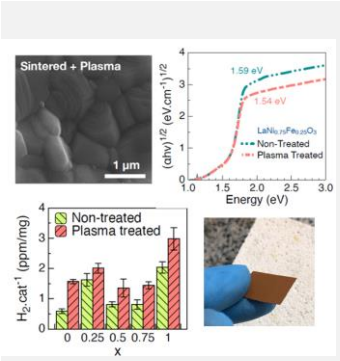

Perovskite oxides, characterized by their ABO_3-type structure, have emerged as highly versatile catalysts owing to the flexibility of their components, abundant availability, and exceptional thermal stability. In this investigation, were assessed the exsolution of the perovskite oxide family $LaNi_xFe_{1-x}O_3$ (x = 0, 0.25, 0.50, 0.75, 1.0), successfully synthesized via the sol–gel method using citric acid and nitrate precursors. The obtained powders were employed to fabricate sintered thin films through tape casting, followed by a post-treatment with plasma. This study systematically explores the sintering parameters, the plasma treatment, and the resulting photocatalytic activity of the $LaNi_xFe_{1-x}O_3$ perovskite oxide.

Introduction

Perovskite is an oxide-based material with advantages such as flexible structure, low cost, and good stability [1]. Due to its extensive range of oxygen stoichiometry, perovskite is an excellent alternative to catalysis applications [2]. Perovskite oxides present active components embedded into the bulk, which could make them a prospective application in energy and environmental areas [3]. Some issues are reported, such as the active nanoparticles inside the bulk structure that can compromise the activity [4].

Compared to traditional methods, exsolution processes have been reported as an excellent alternative to improve catalytic efficiency in perovskite material. Unlike nanoparticles deposited or infiltrated, the exsolved nanoparticles are anchored in the host oxide, providing more agglomeration resistance and carbon poisoning [5,6]. The method consists of making the perovskite matrix nanoparticle emerge on the material's surface through a reduced atmosphere and high temperatures, for example.

Plasma has already been reported as an effective method for exsolving perovskite nanoparticles. It is a partially ionized gas containing radicals, excited-state species, electrons, and ions. Inert species can become very reactive due to the additional internal energy transmitted to atoms and molecules. Plasma has been used as a reducing radical supplier (reducing chemical agents) and delivered to a heated substrate to promote exsolution [7,8].

This work aims to synthesize a perovskite with the formula $LaNi_xFe_{(1-X)}O_3$. Cold plasma was applied to the perovskite surface, and the efficiency of exsolution will be analyzed using catalysis.

Material and Methods

The catalysts, with the formula $LaNi_xFe_{1-x}O_3$ (with x = 0, 0.25, 0.5, 0.75, and 1.0), were synthesized using the citric acid sol-gel method with nitrates. The clarified solution obtained was moved to an oven at 120 °C for 12 h at a 5 °/min rate, then sintered at 700 °C for 7 h.

The suspension was a mixture of the solvent (water), dispersant, and solids contents (35 %) for tape casting. Polyvinyl alcohol was added as a binder (25%). A small amount of surfactant and antifoams was added. The tape casting was done at room temperature onto a silica-coated polyethylene terephthalate carrier film. The doctor blade was adjusted to 1.0 mm thickness and a constant speed at 46.5 cm min−1. The tape was cut and sintered in a ramp of 300 °C for 30 min, 450 °C for 30 min, and 1200 °C for 120 min, a total of 3 hours in a sintering treatment.

The plasma treatment was performed in a cold plasma under argon atmosphere. The plasma was fixed at 199 W at 1 millibar of pressure, and the treatment times were 15 min.

The hydrogen production was analyzed in a quartz reactor in an ethanol/deionized water photo-reform reaction for 60 min using a visible light lamp. The hydrogen produced was transported to an H_2 sensor MQ-8 using a Tygon® E-3603 tubing. Arduino UNO was used to measure the gas produced.

X-ray diffraction (XRD) characterized the crystalline phases. Scanning electron microscopy (SEM) investigated the morphology and sizes of perovskite materials. Zeta potential and Differential reflectance spectroscopy (DRS) analysis were also performed.

Results and Discussion

The perovskite composition was well done. The XRD analysis (Figure 1) confirmed the presence of the perovskite phase of all compositions.

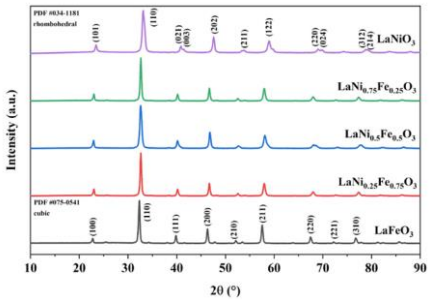

Figure 1. XRD patterns for synthesized perovskites.

The SEM images (Figure 2) show the $LaNi_{0.75}Fe_{0.25}O_3$ composition. The surface presents a roughness when subjected to plasma treatment.

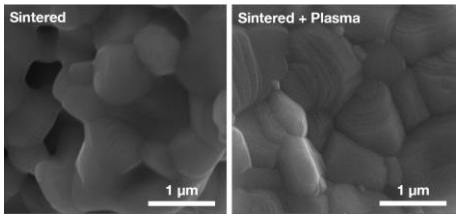

Figure 2. SEM of perovskite sintered and sintered followed by plasma treatment.

DRS of all composition presented a bandgap between 1.56 to 1.65 eV (Figure 3a). The plasma treatment caused a decrease in bandgap of $LaNi_{0.75}Fe_{0.25}O_3$ composite (from 1.59 to 1.54 eV).

Under visible light irradiation, the photocatalytic activity increases the lower the bandgap value. The hydrogen production was evaluated in a ethanol-water photo-reform semi batch reactor. The system was maintained for 60 min and Arduino measured data every 90 s. The average hydrogen production was 1.5 ppm/mg of catalyst (Figure 3b).

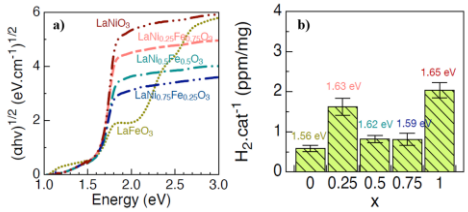

Figure 3. (a) DRS of all compositions of produced perovskite and (b) photo-reform of all perovskites.

The H_2 production exhibits continuous behavior in the 60-minute experiment (Figure 4). The plasma presents more photoactivity (pink curve). As studied before, the oxygen species of the perovskite structure are activated by plasma energy, which can enhance the photoactivity [9].

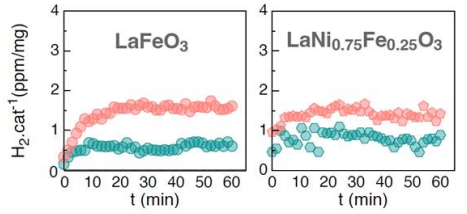

Figure 4. Photo-reform of $LaNi_{0.75}Fe_{0.25}O_3$ with and without plasma.

Conclusions

Hydrogen is a possible alternative to replace fossil fuels, and research in this area is fundamental to its development. Perovskites with $LaNiFeO_3$ composition were successfully produced in this work. The tapes were manufactured, and the material presented photoactivity and showed an amplified response with plasma treatment. The hydrogen production was analyzed in an ethanol photo-reform reaction, and the material proved to be an alternative to this process under visible light.

Acknowledgments

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