

Enhanced Photocatalytic Hydrogen Production from Glucose Aqueous Solution Using Nickel Supported on LaFeO₃

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Nowadays one of the topics of greatest interest to the scientific community is the search for new eco-friendly technologies that allow the production of energy. In particular, one of the main players in this area is hydrogen. Several innovative processes are proposed in the literature for the production of hydrogen. One of these is the heterogeneous photocatalysis. Furthermore, it is also interesting to evaluate the source from which hydrogen is obtained. An interesting solution is glucose, one of the most familiar biomass, which can be used to produce hydrogen from a photocatalytic process. For this reason, in this work we propose the use of Ni as active phase supported on LaFeO₃ photocatalyst for the renewable H₂ production from glucose aqueous solution. Perovskite photocatalysts are quite encouraging materials for H₂ production from aqueous solution owing to their stability in water. Low-cost nickel can be used to improve the performance of perovskites, modifying their surface and thus avoiding the use of expensive noble metal based cocatalysts. Specifically, the LaFeO₃ catalyst was prepared by solution combustion synthesis using citric acid as organic fuel. A specific amount of Ni was deposited on LaFeO₃ surface by chemical reduction method, using sodium borohydride (NaBH₄) as a reducing agent. The prepared samples were characterized by different techniques, such as XRD and UV-Vis. The photocatalytic tests were carried out in a pyrex cylindrical reactor equipped with a N₂ distributor device and irradiated by four UV lamps (emitting at 365 nm) positioned at the same distance from the external surface of the reactor (about 30 mm). The tests were realized with a solution volume equal to 80 ml, an initial concentration of glucose equal to 5550 μmol L⁻¹ and a catalyst dosage equal to 1.5 g L⁻¹. The experimental results evidenced that the presence of Ni on LaFeO₃ surface enhanced the H₂ production and in particular the highest hydrogen production (about 2242 μmol L⁻¹ after 4 h of irradiation time) was obtained with Ni/LaFeO₃, whereas the raw LaFeO₃ was able to produce a lower H₂ amount (about 1394 μmol L⁻¹ after the same irradiation time).

1. Introduction

Hydrogen (H₂) is an alternative fuel that can be produced by means of different ways. Hydrogen is not found in free form (H₂) but must be liberated from molecules such as water or methane. Most hydrogen today is made by steam reforming (Ricca et al., 2017) of natural gas or coal gasification, both with carbon dioxide (CO₂) emissions. Future demand will primarily be for zero-carbon hydrogen (Renda et al., 2020). Hydrogen can also be produced from water through electrolysis (Burton et al., 2021). This process is more energy intensive but can be done using renewable energy, such as wind or solar, and avoiding the harmful emissions associated with other kinds of energy production. If the production of hydrogen from water is considered, it is impossible not to refer to the water splitting process obtained through the application of heterogeneous photocatalysis (Xiao et al., 2020). The photocatalytic process is extremely interesting due to the mild conditions in which it occurs. Literature data (Kawai and Sakata, 1980) report that, in order to increase the performance of the water splitting process, the addition of electron donors considered to react irreversibly with photogenerated h⁺ was proposed (Kurenkova et al., 2020). Several compounds are used as electron donors, such as the Na₂S/Na₂SO₃ system (Kozlova and Parmon, 2017), alcohols (Husin et al., 2018), aldehydes (Puga, 2016) and saccharides (Kondarides et al., 2008). Saccharides are of particular interest since they are the main constituents of biomass (Kurenkova et al., 2020). In particular, an interesting source of sugars is represented

by food industry wastewaters, which if properly treated, could be a raw material for the photocatalytic hydrogen production (Iervolino et al., 2018). As regards the photocatalysts, several semiconductors have been employed for this purpose from TiO_2 (Bahadori et al., 2020) to semiconductors such as CdS (Wang et al., 2020). Recently, perovskites are most requesting semiconductor photocatalysts belonging to very important family of materials and exhibit exceptional response towards photocatalytic application. Among the perovskites, LaFeO_3 has already been studied for the hydrogen production starting from aqueous solutions containing glucose (Iervolino et al., 2016a). In order to increase the photocatalytic performance, it is possible to foresee the use of doping elements (Vaiano et al., 2017) or the presence of noble metals on the surface of photocatalyst (Wang et al., 2020). An interesting alternative to the use of expensive metals could be the use of Ni. In literature the use of this element (Ni) to improve the photocatalytic hydrogen production has been proposed. In particular, the performance of photocatalysts, such as Ni/La-NaTaO_3 where Ni is loaded on the surface of La-NaTaO_3 , was reported (Husin et al., 2018) for the hydrogen production starting from ethanol aqueous solution. The photocatalytic performance of Ni/TiO_2 was evaluated by photocatalytic degradation of methyl orange solution under UV and sunlight irradiation (Liu et al., 2014). Photocatalytic activity of anatase-type TiO_2 nanoparticles with Ni, prepared by gel-sol method, was evaluated for hydrogen production from ethanol aqueous solution (Kimijima et al., 2010). From literature data, it is therefore understood that Ni is an interesting element whose use allows to increase the performance of various types of semiconductors. However, to our knowledge there are no literature data about the use of Ni to improve the performance of LaFeO_3 . For this reason, the aim of this work was to investigate the performance of Ni-modified perovskite LaFeO_3 synthesized with an innovative method of impregnation-reduction, for the photocatalytic hydrogen production from aqueous solution containing glucose.

2. Experimental

2.1 Photocatalysts preparation and characterizations

LaFeO_3 was synthesized following the combustion flame synthesis (Iervolino et al., 2016b). In detail, lanthanum nitrate and iron nitrate as precursor salts in aqueous solution were used, to which a specific amount of citric acid, used as organic fuel, was added. The solution was kept under continuous stirring at a temperature of 60°C for 30 min. An appropriate amount of NH_3 was added to the solution to obtain a pH equal to 7. The solution was dried at 130°C and calcined for 3 h at 300°C . Ni/LaFeO_3 photocatalysts were synthesized by a deposition method using NaBH_4 as reducing agent following the procedure proposed by Kaplan et al. (Kaplan et al., 2011). For this scope, a suitable amount of NiCl_2 was used, obtaining two different sample with 0.18 and 0.25 Ni wt%. The prepared samples were characterized using two techniques. In particular, the X-ray diffraction patterns were obtained with an X-ray diffractometer (Assing), using Cu-K α radiation and the UV-vis reflectance spectra of powder catalysts were recorded by a Perkin Elmer spectrometer Lambda 35 using an RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). Using the UV-vis reflectance spectra the photocatalyst's equivalent band gap energies were determined by back extrapolation of the tangent to the steepest point of the Kubelka-Munk function photocatalyst's equivalent band gap were determined by the Kubelka-Munk function $F(R^\infty)$ by plotting vs. $h\nu$ (Zuorro et al., 2019).

2.2 Photocatalytic activity tests

The efficiency of the prepared photocatalysts, in terms of hydrogen production, was evaluated during photocatalytic tests on glucose aqueous solutions. The efficiency of the prepared photocatalysts, in terms of hydrogen production starting from glucose aqueous solutions, was evaluated during photocatalytic tests. Specifically, the experiments were conducted in a cylindrical pyrex reactor (ID = 2.5 cm) equipped with a peristaltic pump necessary for the recirculation of the suspension in the reactor and for the continuous mixing of the glucose aqueous solution. A specific nitrogen flow rate ($0.122 \text{ NL min}^{-1}$) is blown into the reactor, and it acts as a carrier for the gases produced during the reaction. Four UV lamps (Philips TL 8W/08 F8 T5/BLB, nominal power of 8 W and emission peak at 365 nm) were used as light sources and positioned around the external surface of the reactor. The schematic representation of the photocatalytic reactor is reported in Figure 1. Typically, 0.12 g of catalyst was suspended in 80 mL of aqueous solution containing $5550 \mu\text{mol L}^{-1}$ of glucose (D+ Glucose VWR, Sigma-Aldrich). The suspension was left in dark conditions for 2 h to reach the adsorption-desorption equilibrium of glucose on the photocatalyst surface, and then the photocatalytic reaction was initiated under UV light for up to 4 h. The analysis of the gaseous phase from the photoreactor was performed by a continuous CO_2 , H_2 and CH_4 analyzers (ABB Advance Optima).

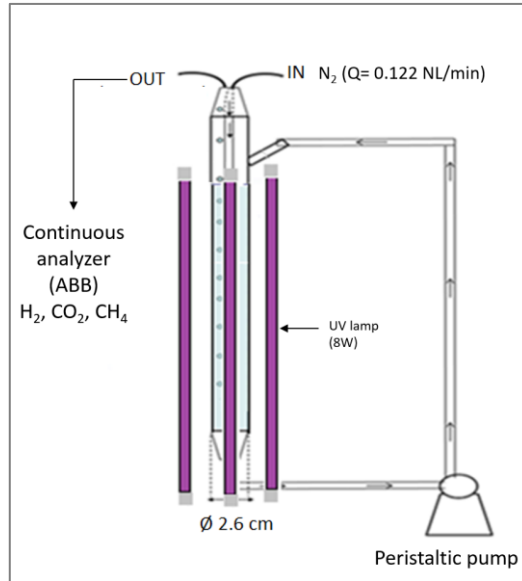


Figure 1: Schematic representation of the photocatalytic reactor

3. Results and discussion

3.1 Photocatalysts characterization

Figure 2 shows the XRD patterns of the LaFeO_3 and $0.18\text{Ni}/\text{LaFeO}_3$ photocatalysts. XRD showed well indexed diffraction peaks, clearly indicating the formation of orthorhombic perovskite type structure for both prepared samples, with the higher intensity peak at 2θ value of 32.16° , which corresponds to LaFeO_3 (h k l) 0 0 2 as for the JCPDS card No. 88-0641, as reported in literature (Tijare et al., 2012). The average crystallite size for these catalysts is about 28 nm, calculated by Sherrer formula (Iervolino et al., 2016b). No significant impurity phases were observed in the XRD spectra. This confirms that the presence of Ni on the LaFeO_3 surface, deposited by the reduction-impregnation method described does not affect the crystal structure of LaFeO_3 .

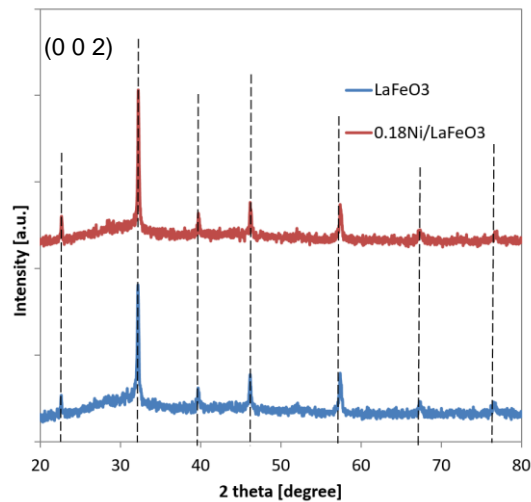


Figure 2: XRD spectra for LaFeO_3 and $0.18\text{Ni}/\text{LaFeO}_3$

Figure 3 (a) shows the reflectance spectra of the prepared samples. As it can be note, the typical absorption band edges of the LaFeO_3 semiconductor was observed at around 814 and 600 nm as the start of the minima of reflectance curves for both the samples and attributed to electron transitions from valence band to conduction band ($\text{O}2\text{p} \rightarrow \text{Fe}3\text{d}$) (Parida et al., 2010). However, for $0.18\text{Ni}/\text{LaFeO}_3$ sample, the absorption band edge at about 600 is less intense than LaFeO_3 and the reflectance value R [%] is higher for wavelength values above 780 nm, and it is lower in the ultraviolet range compared to that measured for LaFeO_3 . The data

obtained from UV–Vis reflectance spectra were used for evaluating the band-gap energy, reported in Figure 3 (b). A band gap value of 2.4 eV is achieved for LaFeO₃ photocatalyst while and a band gap value of 2.35 eV was observed for 0.18Ni/LaFeO₃ sample. The presence of Ni on the perovskite surface therefore also induces a modification in the band gap of the catalyst.

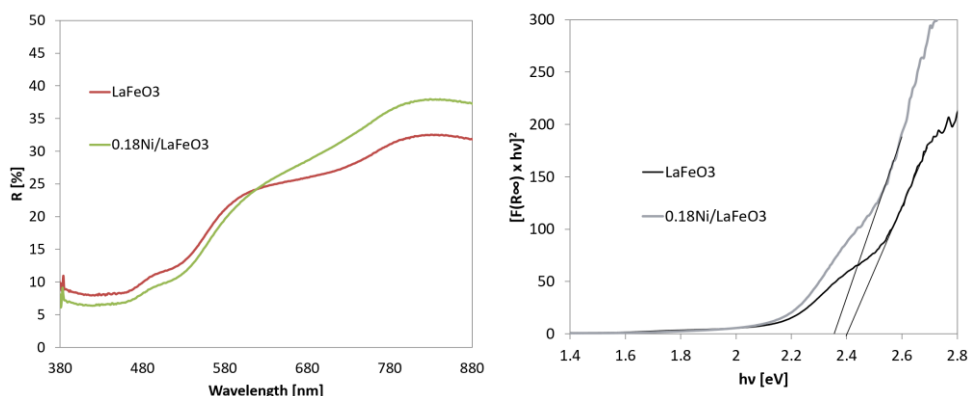


Figure 3: UV-vis DRS spectra (a) and band gap evaluation (b) for LaFeO₃ and 0.18Ni/LaFeO₃ samples.

3.2 Photocatalytic results

3.2.1 Influence of Ni loading on catalyst surface

The influence of Ni amount on LaFeO₃ surface, in terms of photocatalytic hydrogen production, is shown in Figure 4. As it can be seen, the presence of nickel improves the photocatalytic production of hydrogen from a solution containing 5550 μmol L⁻¹ of glucose. It can be observed that after 4 hours of UV irradiation, 2242 μmol L⁻¹ of hydrogen was obtained with 0.18Ni/LaFeO₃ while in the case of using LaFeO₃ 1340 μmol L⁻¹ of hydrogen was produced. It is important to underline the Ni amount used for the 0.18Ni/LaFeO₃ catalyst is very low, even lower than what is usually reported in the literature (Chen et al., 2015). Moreover, Figure 4 shows that with the 0.25Ni/LaFeO₃ catalyst, the production of hydrogen is lower than that obtained with the 0.18Ni/LaFeO₃ sample. In fact, after 4 h of UV irradiation, the photocatalytic hydrogen production was equal to about 1780 μmol L⁻¹ with 0.25Ni/LaFeO₃. So, at Ni loadings above 0.18 wt.%, the H₂ production decreased. The decrease in the activity of the Ni/LaFeO₃ photocatalysts above the optimal Ni loading of 0.18 wt.% may be due to the excessive blockage of LaFeO₃ photoactive sites by the highly dispersed metallic Ni nanoparticles (Chen et al., 2015). Moreover, the finding that the 0.18Ni/LaFeO₃ photocatalyst shows very good activities for H₂ production at low metal loadings is a very promising result for future large-scale photocatalytic hydrogen production technologies. This interesting result highlights that metallic Ni promotes H₂ generation through suppressing electron – hole pair recombination in LaFeO₃ semiconductor, as also confirmed by literature about the use of Ni on TiO₂ surface for hydrogen production from aqueous solution (Chen et al., 2015).

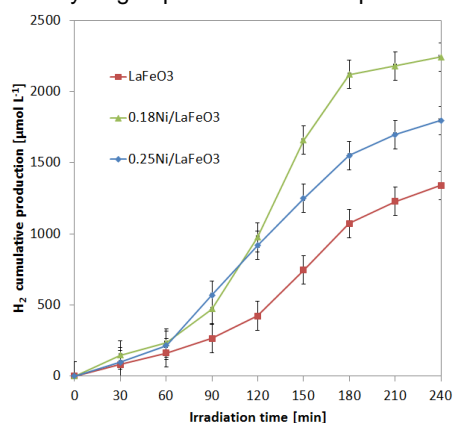
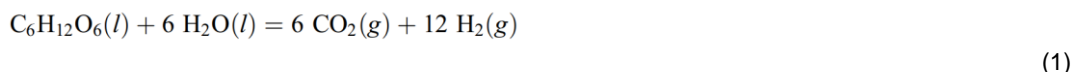
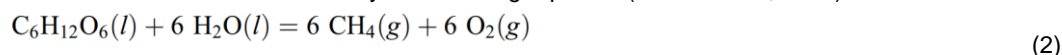


Figure 4: Photocatalytic hydrogen production for LaFeO₃, 0.18Ni/LaFeO₃ and 0.25Ni/LaFeO₃ during UV irradiation time. Glucose initial concentration: 5550 μmol L⁻¹. Catalyst dosage: 1.5 g L⁻¹

Also the CO₂ and CH₄ production was observed during the reaction time (Figure 5). In details, about 50 and 60 μmol L⁻¹ of CO₂ and CH₄ were obtained for LaFeO₃ and about 70 and 65 μmol L⁻¹ of CO₂ and CH₄ for 0.18Ni/LaFeO₃ photocatalyst, after 4 h of UV irradiation. It is interesting to note that for the 0.18Ni/LaFeO₃ photocatalyst the CO₂ production was very similar to CH₄ production while for the LaFeO₃ sample the CO₂ amount obtained after 4 h of UV irradiation time, was lower than the CH₄ amount. The CH₄ and CO₂ production, together with the production of H₂ in a photocatalytic process starting from aqueous solutions containing glucose, has already been observed in previous works (Vaiano et al., 2015). In particular, CO₂ and H₂ could be mainly produced from the photocatalytic wet reforming of glucose, according to the following reaction (Vaiano et al., 2015):



Whereas methane can be formed by the following equation (Vaiano et al., 2015):



However, further studies are necessary to assess the reaction mechanism and to evaluate the presence of any reaction by-products in the liquid phase. The obtained results confirm that the presence of metallic Ni dispersed on the surface of LaFeO₃ contributes to an improvement in hydrogen production.

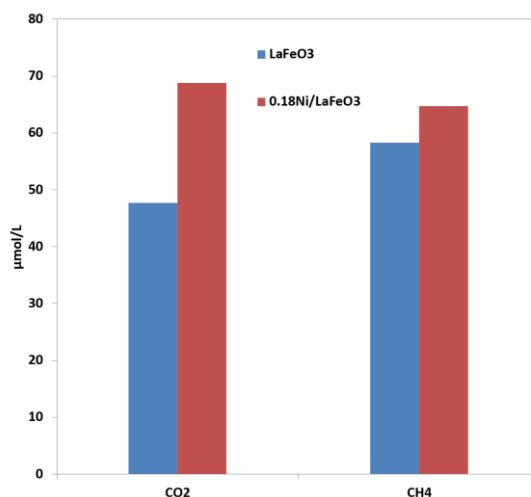


Figure 5: Photocatalytic CO₂ and CH₄ production for LaFeO₃ and 0.18Ni/LaFeO₃ during UV irradiation time. Glucose initial concentration: 5550 μmol L⁻¹. Catalyst dosage: 1.5 g L⁻¹

4. Conclusions

The results reported in this work show that small quantities of Ni, dispersed on the perovskite surface, are needed to obtain improvements in terms of H₂ production under UV light. In fact, the optimal nominal Ni loading is 0.18 wt%, which afforded H₂ production equal to 2242 μmol L⁻¹ after 4 h of UV irradiation from 5550 μmol L⁻¹ of glucose in aqueous solution. The XRD results confirm that Ni is dispersed on LaFeO₃ since no variation of the crystal lattice of LaFeO₃ appears. Furthermore, the presence of Ni on the LaFeO₃ surface involves a modification of the UV-vis spectrum which results in a different ability to absorb defined wavelengths for the 0.18Ni/LaFeO₃ catalyst, which seems to absorb UV light more intensely. Overall, it is possible to confirm that Ni/LaFeO₃ photocatalyst is a possible low-cost alternative to noble metal-based photocatalysts for H₂ production from glucose aqueous solution.

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