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Photocatalytic Conversion of Glucose to H_2 over $LaFeO_3$ Perovskite Nanoparticles

Giuseppina Iervolino[a*], Vincenzo Vaiano[a], Diana Sannino[a], Luigi Rizzo[b], Paolo Ciambelli[a]
[a] Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy
[b] Department of Civil Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano (SA) Italy
giiervolino@unisa.it

The aim of this work was to evaluate the influence of operating conditions in the photocatalytic hydrogen production from glucose solution on $LaFeO_3$ nanoparticles under UV and visible through light-emitting diodes (LEDs). In particular, $LaFeO_3$ prepared by solution combustion synthesis with a specific amount of citric acid used as fuel, has been tested. The process efficiency was evaluated in terms of both glucose degradation and hydrogen production during the irradiation time. The influence of initial glucose concentration, catalyst dosage, and light source has been evaluated. Experimental results showed that the initial concentration of glucose affected the photocatalytic hydrogen production, and in particular the hydrogen production increased linearly (up to 370 μmol) as glucose concentration was increased up to 1000 mg L^{-1}. Moreover, 1.5 g L^{-1} was found to be the optimum value for the catalysts dosage for obtaining the best photocatalytic hydrogen production after 4 h of irradiation. Furthermore, $LaFeO_3$ nanoparticles were active in the production of hydrogen also under visible light.

1. Introduction

H_2 is potentially a major fuel for internal combustion engines and fuel cells in the future because of its high-energy efficiency and clean burning properties. However, H_2 is currently produced via steam reforming of non renewable fossil fuels, such as coal, natural gas, and petroleum (Song, 2002). Interestingly, biomass-derived substrates, such as alcohols or carbohydrates, may be used for hydrogen production particularly in the case of waste materials (sewage from food, wine, or paper industry) (Colmenares et al., 2011), simultaneously helping to clean wastes (without disposal costs) and to produce a highly valued fuel (Rossetti, 2012).
Some wastewaters from food industry processes contain a high concentration of sugars, particularly glucose, which should be removed before effluent disposal or reuse**,** but, if properly treated, could be a raw material for hydrogen production by photocatalytic process (Wu et al., 2008).
Therefore, the photocatalytic way for the production of hydrogen through reforming of organic compounds present in wastewater could be a very interesting clean route.
Titanium dioxide was the first material investigated for water splitting reaction but various other photocatalysts, like mixed oxides (Dholam et al., 2009), TiO_2 nanotube (Ampelli et al., 2011) and perovskites (Parida et al., 2010) have been widely studied for the photocatalytic hydrogen generation. Perovskite photocatalysts are quite encouraging materials for water splitting owing to their stability in water.
$LaFeO_3$ is one of the most common perovskite type oxides and a promising material with abundance of functionalities, having a general formula ABO_3, where position A is occupied by the rare earth ion, and position B by the transition metal ion. $LaFeO_3$ displays significant physical and chemical properties making it of great importance to be used in advanced technologies such as solid oxide fuel cells catalysts (Arendt et al., 2008), chemical sensors (Zhang et al., 2006), photocatalysis (Su et al., 2010) and biosensors (Thirumalairajan et al., 2012).
Perovskite type photocatalysts are quite encouraging materials for water splitting owing to their stability in water. The excellent catalytic activity of $LaFeO_3$ is well known, because of its high stability, non-toxicity and small band gap energy (about 2.07 eV) (Dhinesh Kumar and Jayavel, 2014). The effectiveness of perovskites

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in the H_2 production via water splitting in the presence of sacrificial agents such as ethanol and noble metals (Pt) as a co-catalyst has been also proved (Parida et al., 2010).
Therefore, the use of $LaFeO_3$ for hydrogen production from water containing sugar (glucose) is an option worthy of investigation.
In this work the effectiveness of $LaFeO_3$ photocatalysts for hydrogen production under UV and visible light emitted by light-emitting diodes (LEDs) has been studied. The influence of different parameters, such as the initial concentration of glucose, the catalyst dosage and the light source, were evaluated.

2. Experimental

2.1 Photocatalyst preparation

$LaFeO_3$ nanoparticles were prepared by solution combustion synthesis, starting from lanthanum nitrate and iron nitrate aqueous solution, to which citric acid used as organic fuel was added. Citric acid, $La(NO_3)_3$ and $Fe(NO_3)_3$ (weight ratio 1/1.03/0.96) were dissolved in 100 ml of distilled water. The solution was kept under continuous stirring at 60 °C. Ammonium hydroxide (Carlo Erba, 37 wt %) was slowly added to adjust the pH of the solution up to 7.0. The solution was dried at 130° C and then calcined at 300 °C for 3 hours to ignite the solution combustion reaction.
The photocatalyst was characterized by different techniques. Specific surface area (SSA) of the samples were evaluated by BET method using N_2 adsorption with a Costech Sorptometer 1042 after a pretreatment at 150 °C for 30 minutes in He flow (99.9990 %). X-ray diffraction patterns were obtained with an X-ray diffractometer (Assing), using Cu-Kα radiation. UV–vis reflectance spectra of powder catalyst were recorded by a Perkin Elmer spectrometer Lambda 35 using a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). Equivalent band gap determinations of the photocatalysts were obtained from Kubelka–Munk function $F(R\infty)$ by plotting $[F(R\infty) \times h\nu]^2$ vs. $h\nu$ (Ciambelli et al., 2009).

2.2 Photocatalytic tests

Photocatalytic experiments of glucose degradation and conversion to hydrogen were carried out with a pyrex cylindrical reactor (ID = 2.5 cm) equipped with a N_2 distributor device (Q=0.122 NL min^{-1}).
Irradiation was provided by a strip of UV-LEDs (nominal power: 10W) with wavelength emission in the range 375–380 nm, or by a strip of visible LEDs with the main wavelength emission at 440 nm (nominal power: 10W) positioned around the external surface of the reactor so that the light source uniformly irradiated the reaction volume.
Typically, 0.12 g of catalyst was suspended in 80 ml of an aqueous solution containing 500 mg $L^{-1}$of glucose. Different catalyst dosage (0.75 and 3 g L^{-1}) and glucose initial concentration (1000, 2000 and 4000 mg L^{-1}) were also used. Continuous mixing of the solution in the reactor was assured by external recirculation of water through a peristaltic pump. 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 reaction was started under UV (or visible) light up to 4 hours. The analysis of the gaseous phase from the photoreactor was performed by continuous CO, CO_2, O_2, H_2 and CH_4 analyzers (ABB Advance Optima). The concentration of glucose was measured by a spectrophotometric method (Dubois et al., 1956).

3. Results and discussion

3.1 Photocatalyst characterization

The solution combustion method allowed to produce $LaFeO_3$ with a specific surface area equal to 18 m^2/g. The XRD pattern of $LaFeO_3$ showed well indexed diffraction peaks (Figure 1), clearly indicating the formation of orthorhombic perovskite type structure, as reported in literature (Tijare et al., 2012). The crystallite size of $LaFeO_3$ (20 nm) has been evaluated by using the Scherrer formula at diffraction line positioned at 2θ value of 32.16 degree, which corresponds to $LaFeO_3$ (0 0 2).
The reflectance spectrum of the sample is shown in Figure 2. The typical absorption band edge of the $LaFeO_3$ semiconductor was observed and attributed to electron transitions from valence band to conduction band ($O_{2p} \rightarrow Fe_{3d}$) (Parida et al., 2010). The data obtained from UV–Vis reflectance spectra were used for evaluating the band-gap energy of $LaFeO_3$. As shown in Figure 3 the band-gap energy was equal to 2.0 eV, indicating that this photocatalyst can be activated also in the presence of visible light irradiation.

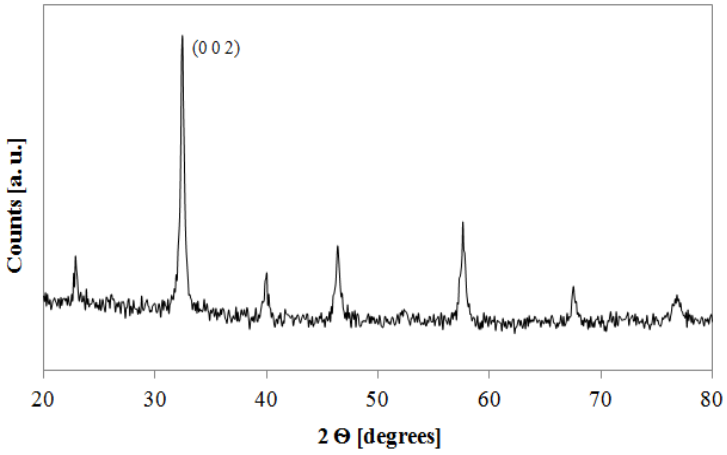

Figure 1: XRD spectrum of $LaFeO_3$.

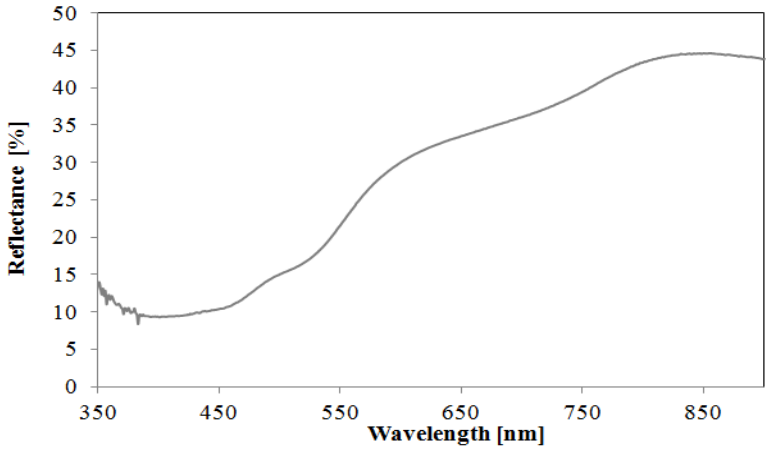

Figure 2: UV-Vis DRS spectrum of $LaFeO_3$ photocatalyst in terms of reflectance as a function of wavelength.

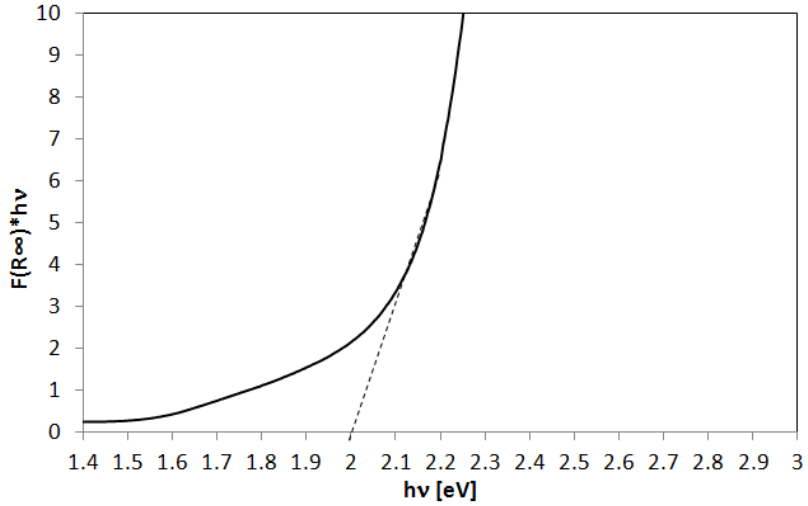

Figure 3: Band-gap energy calculation for $LaFeO_3$ photocatalyst.

3.2 Photocatalytic results

Figure 4 shows the influence of the initial glucose concentration on hydrogen production and glucose degradation during the UV irradiation time. By increasing the initial concentration of glucose in solution, hydrogen production increased (Figure 4a). In particular, at 500 and 4000 mg L^{-1} of glucose, 190 and 460 µmol of hydrogen after 4 h of irradiation were obtained, respectively (Figure 4a).
Moreover, the highest sugar degradation was obtained with 1000 mg L-1 glucose initial concentration (Figure 4b). Figure 5 reports the trend of hydrogen production and glucose degradation after 4 h of UV irradiation, as a function of the initial concentration of glucose in solution. It is worthwhile that, as the initial concentration of glucose was increased, a linear increase of hydrogen production up to 1000 mg L^{-1} of initial concentration of glucose was observed.
The same behavior was found for glucose degradation. Every further increase of the initial concentration of glucose did not result in a linear increase of the hydrogen production, and glucose degradation was almost unchanged. This typical kind of Langmuirian catalytic behavior suggests that the reaction depends of the glucose concentration on the catalyst surface rather than of the concentration in the solution (Fu et al., 2008).
The influence of catalyst dosage on glucose conversion and hydrogen production after 4 h of UV irradiation was also evaluated (Figure 6). The photocatalytic efficiency increased as the catalyst loading was increased up to 1.5 g L^{-1}. Further increase of catalyst loading resulted in a decrease of glucose conversion (Figure 6a) and H_2 production (Figure 6b). The presence of an optimal value for the catalyst dosage is likely related to the limiting effect of the interception of the light by the suspension on the degradation rate (Vaiano et al., 2015).
Finally, the effect of different light sources in hydrogen production and glucose degradation on $LaFeO_3$ was evaluated.

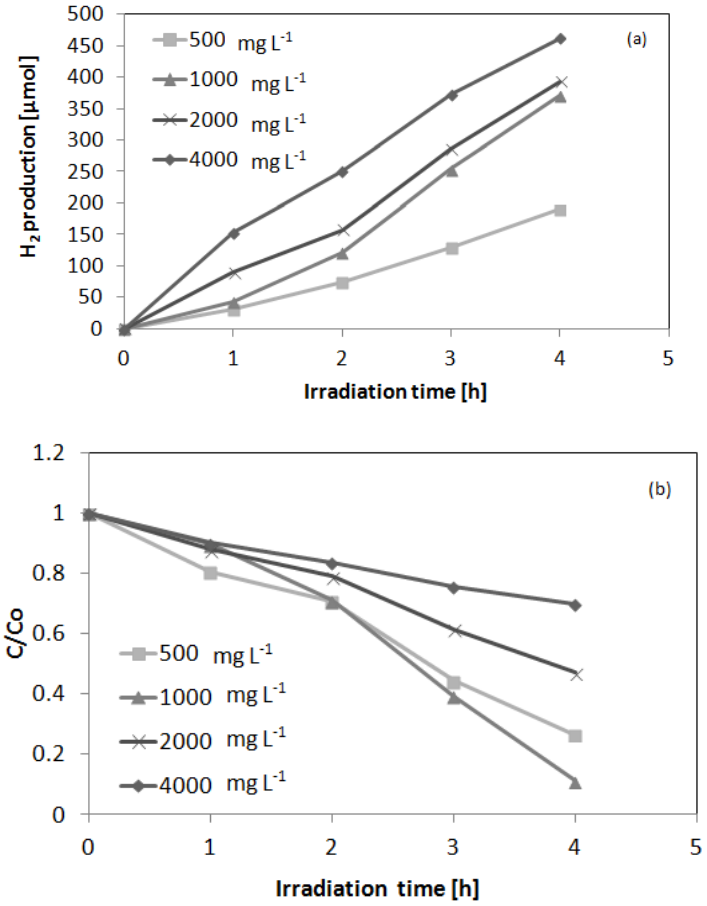

Figure 4: Influence of the initial glucose concentration on hydrogen production (a) and glucose degradation (b), during the irradiation time under UV-LEDs. Catalyst dosage: 1.5 g L^{-1}.

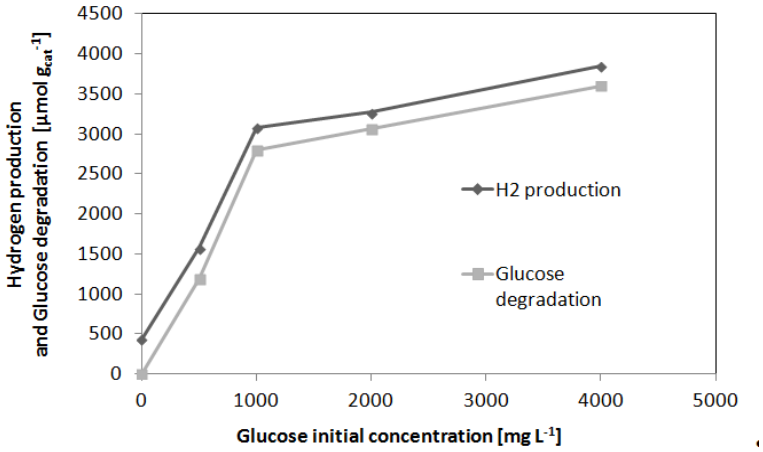

Figure 5: Trend of hydrogen production and glucose degradation after 4 h of UV irradiation, as a function of the initial concentration of glucose in solution. Catalyst dosage: 1.5 g L^{-1}.

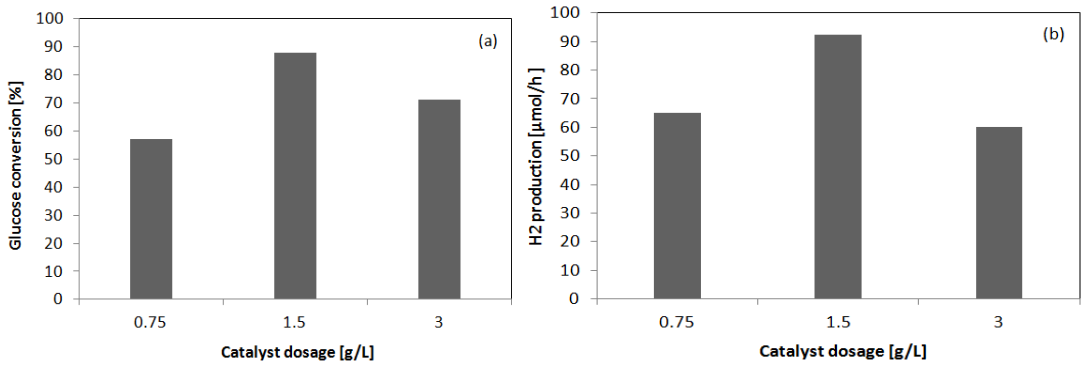

Figure 6: Influence of catalyst dosage on glucose conversion (a) and hydrogen production (b) after 4 h of irradiation time; Light source : UV LEDs.; Glucose initial concentration : 1000 mg L^{-1}.

The comparison between the two different light sources (UV and visible light) on the behaviour of glucose normalized concentration and hydrogen production during the irradiation time is shown in figure 7. According to UV-Vis DRS results (Band gap equal to 2.0 eV) reported in Figure 2, this catalyst is active also in the presence of visible light, as also reported in literature for the photocatalytic water splitting (Tijare et al., 2012). In particular, after 4 h of irradiation by visible LEDs, H_2 production of 179 µmol and glucose degradation of about 43% were achieved.

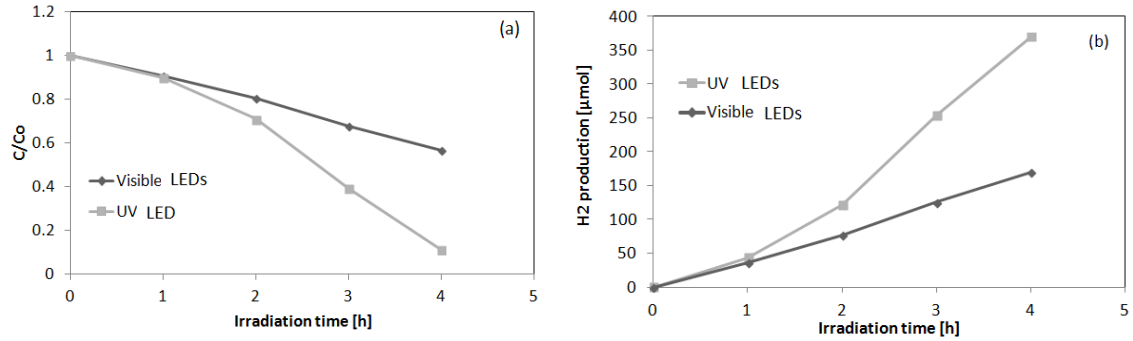

Figure 7: Influence of different light source (UV and Visible) on glucose degradation (a) and hydrogen production (b); Catalyst dosage: 1.5 g L^{-1}; Glucose initial concentration:1000 mg L^{-1}.

4. Conclusion

We have synthesized a $LaFeO_3$ perovskite photocatalyst by the solution combustion synthesis method, using a specific amount of citric acid as organic fuel. The experimental results obtained in the photocatalytic hydrogen production by glucose degradation have shown that the initial concentration of glucose in solution influences the hydrogen production. An interesting result was obtained by tuning the catalyst dosage, a critical parameter controlling the efficiency of the photocatalytic treatment. In particular, it was found that the best catalyst dosage is 1.5 g L^{-1}. The effect of different light sources was evaluated, showing a significant photocatalytic activity of $LaFeO_3$ under visible light for hydrogen production. In particular, under visible light source, the hydrogen production was equal to 179 μmol with glucose degradation equal to about 43%.

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