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Enhanced photocatalytic hydrogen production from glucose aqueous matrices on Ru-doped $LaFeO_3$

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ABSTRACT

In the present work, the renewable hydrogen production by the photocatalytic degradation of glucose over Ru-doped $LaFeO_3$ photocatalysts under UV or visible irradiation has been assessed for the first time. The perovskite doped with ruthenium was successfully synthesized by solution combustion synthesis. The effects on the hydrogen production and glucose degradation of reaction parameters, such as amount of ruthenium, initial concentration of glucose, reactor configuration and light source were systematically investigated. The results showed that the photocatalytic H_2 production from the glucose solution can be significantly enhanced (2179 $\mu mol/g_{cat}$ after 4 h of UV irradiation) using a specific amount of ruthenium (0.47 mol% of Ru) in $LaFeO_3$. Moreover, photocatalytic performances were strongly affected by reactor configuration; the comparison between two cylindrical reactors with different diameters showed improved performances in the reactor with the smaller diameter due to the enhanced photons flow that intercepts the photocatalysts particles dispersed into the glucose solution. In particular, under UV light, the hydrogen production increased from 2179 to 3474 $\mu mol/g_{cat}$ and the glucose degradation was complete after 3 h of irradiation.

Finally, the optimized photocatalyst was also tested under visible light on a real wastewater taken from a brewing process; the results showed an interesting hydrogen production as high as 2128 $\mu mol/g_{cat}$ (after 4 h of visible irradiation). In conclusion, this work further supports the interesting perspectives in the applicability of the photocatalytic process for the valorization of wastewater with the aim to obtain hydrogen from the degradation of target organic compounds.

1. Introduction

In recent years, the limited availability of fossil fuels and the increasing environmental pollution derived from their use as main source of energy has led to the development of new technologies for the production of zero environmental impact energy vectors such as hydrogen [1]. Hydrogen is a storable, clean and environmentally friendly fuel whose combustion results in the solely generation of water, with no emissions of atmospheric pollutants, greenhouse gases or particulates. However, about 95% of hydrogen currently derives from fossil fuels, mainly by steam reforming of natural gas and petroleum, while the remaining 5% comes from the electrolysis of water [2]. Because these processes involve the use of nonrenewable resources or high energy consumption, the corresponding routes of hydrogen production are not sustainable or economically feasible. Over the last few years, biomass, mainly glycerol, has been used to produce hydrogen by different methods, such as steam reforming [3], gasification [4], autothermal reforming [5] and electrochemical reforming [6]. Alternatively, hydrogen can be also produced from biomass in mild conditions (room temperature and atmospheric pressure) through heterogeneous photocatalysis [2].

Photocatalysis has been extensively studied for environmental remediation (i.e., pollutant degradation) and solar energy conversion (i.e., hydrogen production and CO_2 reduction) [7–15]. Up today, the photocatalytic production of hydrogen can be obtained mainly by two processes, i.e. either by the direct splitting of water into H_2 and O_2, or by the photo-reforming of organic compounds [16–22]. In many studies regarding the photocatalytic production of H_2, different substances (e.g., organic acids, alcohols, sulfide/sulfite) acting as electron donors, have been generally used [23–26]. However, this approach requires the use of sacrificial agents in order to get a good hydrogen production, which makes the process expensive. On the contrary, if the organic pollutants present in wastewater are seen as electron donors for H_2 produc-

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tion, the overall process may be potentially cost-effective. Glucose is the most diffused and cheapest carbohydrate as it can be directly obtained from cellulose, the most abundant and renewable biomass on Earth. It is used for ethanol or butanol production, a wide variety of useful bio-based chemicals as industrial feedstocks for bioplastics and also to obtain hydrogen [27]. But glucose is also present at high concentration in wastewaters from some agro-food industries. Accordingly, the heterogeneous photocatalysis applied to wastewater treatment offers the opportunity to simultaneously recovery valuable products (such as hydrogen and methane) to be converted into energy [28–30]. Moreover, photocatalytic technology can be also operated under natural sunlight [31] so drastically cutting energy costs down. The most widely used semiconductor in photocatalysis is TiO_2 because of its physical and chemical properties, excellent stability, high availability and low cost [32]. With regard to the photocatalytic hydrogen production, the use of semiconductor (such as TiO_2 or ZnO) doped with nobles metals (Au, Pt, Pd) has been extensively reported [28,33–38]. Alternatively, $LaFeO_3$, one of the most common perovskite type oxide, has a general formula ABO_3, where position A is occupied by the rare earth ion (La^{3+}), and position B by the transition metal ion (Fe^{3+}). $LaFeO_3$ (conduction band potential = 0.025 eV [39]) has shown excellent photocatalytic activity because of its interesting properties such as high stability, non-toxicity and small band gap energy (2.07 eV), that qualify this perovskite as visible light active photocatalyst [40,41].

Generally, the functional properties of perovskite materials can be controlled either by modulating the crystalline structure or by the incorporation of different metal ions into the perovskite lattice [42]. $LaFeO_3$ powders doped with Sr and Cu have been recently tested in a photoelectrochemical process [42].

However, studies about the photocatalytic hydrogen production from aqueous solution on doped $LaFeO_3$ systems are still lacking in the literature. Among the several possible dopants for perovskites, ruthenium is the most suitable since a large amount of Ru^{3+} ions can be introduced within the perovskite network (in particular by replacing the transition metal cation of the perovskite) keeping it single-phase [43].

Therefore, in this work Ru-doped $LaFeO_3$ samples were synthesized and characterized and their effectiveness in the photocatalytic hydrogen production from glucose aqueous matrices has been assessed for the first time. The influences of Ru loading and photoreactor configuration have been analyzed. Finally, the optimized photocatalyst was also tested under visible light on a real wastewater taken from a brewing process.

2. Experimental

2.1. Synthesis of photocatalysts

Ru-$LaFeO_3$ samples were prepared by solution combustion synthesis, using citric acid as organic fuel and metal nitrate as metal precursor (oxidizer) [44]. In detail, 1.66 g of $Fe(NO_3)_3{\cdot}9H_2O$ (Riedel-deHaen, 97 wt%), 1.78 g of $La(NO_3)_3{\cdot}6H_2O$ (Fluka, 99%), 0.86 g of citric acid (Fluka, 99 wt%) and a specific amount of $RuCl_3$ (Sigma Aldrich, 99%) used as dopant, were completely dissolved in 100 mL of bidistilled water. The solution was kept stirred continuously at 60 °C for 5 min. Then, ammonium hydroxide (Carlo Erba, 37 wt%) was slowly added to regulate the pH of the solution up to 7.0. The solution was dried at 130° C and then calcined at 300° C for 3 h in static air using a muffle furnace to ignite the solution combustion reaction [41]. Different amounts of $RuCl_3$ were used for the doping of $LaFeO_3$ to obtain photocatalysts with different amounts of Ru (Table 1). The Ru nominal loading is expressed as molar percentage and it was evaluated through Eq. (1):

$$\%molRu = \frac{nRu}{nLa + nFe} \cdot 100 \quad (1)$$

Where: nRu is the number of moles of $RuCl_3$ used in the synthesis;

nLa is the number of moles of $La(NO_3)_3{\cdot}6H_2O$ used in the synthesis;

nFe is the number of moles of $Fe(NO_3)_3{\cdot}9H_2O$ used in the synthesis.

2.2. Photocatalysts characterization

Different techniques were used to characterize the photocatalysts. In particular the crystallite size and crystalline phase of Ru-$LaFeO_3$ photocatalysts were studied with an X-ray diffractometer (Assing), using Cu-Kα radiation. Total Ru content of the samples were determined by X-ray fluorescence spectrometry (XRF) in a thermoFischer ARL QUANT'X EDXRF spectrometer equipped with a rhodium standard tube as the source of radiation and with Si-Li drifted crystal detector. The specific surface area analysis was performed by BET method using N_2 adsorption with a Costech Sorptometer 1042 after a pretreatment at 150 °C for 30 min in He flow (99.9990%). The Raman spectra of the samples were recorded with a Dispersive MicroRaman system (Invia, Renishaw), equipped with 785 nm diode-laser, in the range 100–1000 cm^{-1} Raman shift. UV–vis reflectance spectra (UV-vis DRS) of powder catalysts were recorded by a Perkin Elmer spectrometer Lambda 35 using a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). All spectra were obtained using an 8° sample positioning holder, giving total reflectance relative to a calibrated standard SRS-010-99 (Labsphere Inc., North Sut-ton, NH). Band-gap energy determinations of the photocatalysts were obtained from Kubelka–Munk function $F(R_\infty)$ by plotting $[F(R_\infty)\ x\ h\ \nu]^2$ *vs.* $h\ \nu$ [45–47]. Scanning electron microscopy (SEM) (Assing, mod. LEO 420) was used to characterize the morphology of the samples at an accelerating voltage of 20 kV.

2.3. Photocatalytic tests

The photocatalytic experiments for hydrogen production from glucose aqueous matrices were carried out in a photocatalytic pyrex cylindrical reactor [10,48,49] (ID = 2.5 cm) (R1) equipped with a N_2

Table 1
Summary of the characterization results.

Catalyst	Ru nominal amount [mol%]	Ru measured amount (XRF) [mol%]	Crystallite size (XRD) [nm]	Specific surface area [m^2/g]	Band gap (UV–vis DRS) [eV]
$LaFeO_3$	0	0	37	4	2.12
0.12% Ru	0.12	0.11	29	5	2.08
0.23% Ru	0.23	0.19	30	5	2.04
0.38% Ru	0.37	0.35	30	5	2.01
0.47% Ru	0.47	0.49	29	5	1.98
0.70% Ru	0.70	0.72	31	5	1.85
1.16% Ru	1.16	1.22	28	5	1.90
2.33% Ru	2.33	2.43	30	5	1.72