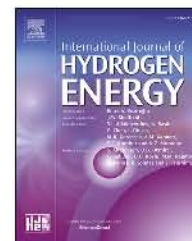


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# Hydrogen production by laser irradiation of metals in water under an ultrasonic field: A novel approach

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## ABSTRACT

An alternative method for hydrogen production by laser irradiation of metals in water is proposed. Metals such as Ti, Al, Mg and Al–Mg alloy and Si, were laser ablated and subjected to an ultrasonic field simultaneously to promote a displacement chemical reaction of hydrogen from water. The produced gas was characterized by gas chromatography and mass spectrometry. Molecular hydrogen was found suggesting that this procedure allows the production of H<sub>2</sub> of high purity. All the studied metals under laser irradiation produced H<sub>2</sub> and the volume rise as the laser fluence was increased following a no-linear monotonic behavior with a similar tendency. Without ultrasound the amount of hydrogen was significantly reduced. An important advantage of the proposed H<sub>2</sub> production method is the low amount of mass consumed which lead to maximum hydrogen production rates close to 1300 ml/min per gr of aluminum.

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## Introduction

Nowadays hydrogen is considered a carrier of clean energy because when used in fuel cells the only generated by-product is water. The hydrogen production has been carried out for many years mainly from hydrocarbons, the most important methods at industrial level are the reforming of natural gas

and the gasification of coal and petroleum coke [1,2]. On the other hand, proton exchange membrane (PEM) electrolyzers of last generation to produce hydrogen, based on the electrolysis of water, can be placed where hydrogen is required although in these systems more energy is needed. However, with these generators large amounts of highly pure hydrogen are produced without emissions of gaseous pollutants such as, for

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example, CO<sub>2</sub>. For this reason, water electrolysis is considered today the most important hydrogen production technology. It must be pointed out that direct decomposition of water is very difficult in normal conditions; for example, the pyrolysis reaction occurs at high temperatures, starting at approximately 3700 °C, and water electrolysis represents only 4% of the world hydrogen production [3]. Therefore, various methods for water splitting have been proposed as the photo-electrochemical and photocatalytic procedures among others [4–6]. Studies on the photocatalytic splitting of water induced by laser irradiation to produce hydrogen and oxygen have been carried out using Fe<sub>2</sub>O<sub>3</sub> as catalyst for splitting with a laser beam source of 355 nm [7]. In this line, a very important issue is to investigate methods to produce hydrogen without the generation of greenhouse gases which can be harmful to human beings and to the environment.

Recently, some chemical reactions of reactive metals with water releasing hydrogen have been investigated in the field of hydrogen energy because of their potential applications in hydrogen production [8]. Particularly, the use of aluminum or its alloys to produce hydrogen from water is considered a promising way. This is due to its thermodynamics properties, aluminum should spontaneously react exothermically with water through a displacement chemical reaction. Depending on temperature, there are three possible reactions of aluminium with water:

- a)  $2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2$ , from room temperature to 280 °C.
- b)  $2\text{Al} + 4\text{H}_2\text{O} \rightarrow 2\text{AlO}(\text{OH}) + 3\text{H}_2$ , from 280 to 480 °C
- c)  $2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2$ , for temperatures higher than 480 °C.

All these reactions produce the same amount of H<sub>2</sub> but require different amounts of water. These also produce different kind of by-products, bayerite, boehmite and alumina respectively.

However, it is well known that a piece of aluminum submerged into water do not produce any reaction under standard conditions. This is because aluminum has strong affinity for oxygen forming a dense oxide layer (Al<sub>2</sub>O<sub>3</sub>) on its surface impeding the reaction. Therefore, the key issue to induce and sustain the reaction of aluminum with water at room temperature is the continuous removal of that alumina layer. Several approaches have been proposed to circumvent the protective layer of aluminum oxide allowing the reaction with water to proceed. Among them the use of aluminum powders activated by ball-milling, followed by their reaction with water with the subsequent hydrogen release has been reported. In this case the maximum production rate is close to 8 ml/min per gr of Al [9]. Chemical methods have been applied as well to remove the oxide layer allowing the reaction to take place [10].

Another alternative are the techniques based on laser irradiation processes. The hydrogen production by laser assisted procedures has been investigated before [11–18]: as an example the photochemical hydrogen generation from charcoal powder and other forms of carbon mixed with distilled water by irradiation with 532 nm nanosecond laser pulses generating a maximum gas volume close to 1.5 mL after 30 min of irradiation has been reported [11]. A

disadvantage of this approach is that the generated gas contains hydrogen, carbon monoxide and carbon dioxide. Furthermore, the activity of pure Fe<sub>2</sub>O<sub>3</sub> catalyst and various electron capture agents, such as Fe<sup>3+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, and Li<sup>+</sup>, in the water splitting process under the irradiation of a laser beam at 355 nm has been investigated [12]. Hameed et al. studied the photocatalytic water splitting for hydrogen production using WO<sub>3</sub> doped with transition metal ions under UV laser irradiation [13]. Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanopowders were reduced efficiently using Nd:YAG pulsed lasers based on laser ablation in liquids for hydrogen production [14]. Ikeda et al. reports on the photocatalytic hydrogen generation from methanol aqueous solution containing a mixture of titanium dioxide (TiO<sub>2</sub>) and graphite silica by laser ablation in liquid [15]. Dehydrogenation and combustion reactions have been promoted from a mixture of carbon-water and graphite-water by irradiating them with nanosecond laser pulses to generate hydrogen using two wavelengths, the amount of gas generated by 532 nm laser pulses was found higher than the one generated by 1064 nm pulses [16]. The splitting of water during plasma electrolysis of drinking water has been found to be enhanced by laser focusing [17]. Another approach consists in the laser irradiation of colloidal solutions of Au nanoparticles suspended in water resulting in the formation of breakdown nanoplasmal with the subsequent emission of H<sub>2</sub>, in this case the H<sub>2</sub> production depends critically on the energy of the laser pulses and on the concentration of Au NPs in the solution [18]. From these references it is evident that the potential of laser radiation to assist methods for hydrogen production without the generation of greenhouse gases is very appealing.

Concerning laser ablation in particular it has been widely used for advanced surface treatments as a process of matter removal under high energy laser pulses. The term laser ablation is used in this work in its more general meaning to describe the process of removing material from the surface of a solid target under irradiation with laser pulses [19]. Among the physical mechanisms involved in the matter removal from the surface of a solid, evaporation/sublimation, phase explosion, mechanical breakdown and photochemical reactions can be mentioned [20]. It has been established that depending on the laser fluence different regimes can be reached; at lower fluences photothermal mechanisms for ablation include material evaporation and sublimation of the superficial layer of the target whereas at higher laser fluences, a significant fraction of the evaporated material may become ionized, producing a plasma [21,22]. Laser wavelength, laser pulse duration, laser energy, and materials properties are the main parameters which determine the laser ablation processes [23]. Laser ablation has been applied successfully in a variety of situations that require to remove superficial layers with good control such as restoration and cleaning of artworks and historical monuments [24], cleaning from radioactive contamination [25], surgery [26,27], among others.

Ultrasound fields are used since a long time for surface cleaning. The physical phenomenon responsible for these ultrasonic processes is the generation of acoustic waves, which transform in pressure waves in a liquid medium that in many cases is water. In the low-pressure regions bubbles are formed. These bubbles grow and suddenly collapse in extreme conditions the phenomenon is known as cavitation [28].



Ultrasonic activity has also been demonstrated to speed or enhance the effect of many chemical reactions. This is probably caused mostly by the high energy levels reached as high pressures and temperatures are attained at the implosion sites. These investigations have given birth a scientific discipline, now widely used, named sonochemistry [29].

It is worth mentioning that the combination of laser ablation in liquids with an ultrasound field has already been investigated for dispersion purposes [30], and it has been reported that it leads to an enhancement of the production rate of the nanoparticles [31]. In previous works, we have reported that ultrasound promotes important changes in the morphology of the nanostructures producing two-dimensional materials in colloidal suspension [32,33]. In this work we use laser ablation combined simultaneously with ultrasound to remove the oxide layer of aluminum and other metals to induce their chemical reaction in presence of water with the consequent release of hydrogen. To our best knowledge this is the first report of this procedure for hydrogen production with promising results.

## Experimental procedure

Experiments were performed by irradiating with a laser beam several targets such as Ti, Si, Al, Mg and an Al–Mg alloy. These materials were selected considering their electronegativity values respect to the electronegativity of oxygen with the purpose of favoring the oxide formation. The metal target was placed inside of a 20 ml glass flask. A ns pulsed Nd: YAG laser with emission at the fundamental line (1064 nm) and working at a repetition rate of 10 Hz was used as energy source. The laser beam was directed perpendicularly to the target surface with a spot size of 6 mm. The energy density was increased from 0.7 to 1.8 J/cm<sup>2</sup> by varying the energy per pulse. These values are below the ablation threshold for plasma formation of the employed metals. For the experiments under ultrasonic field, the flask was placed inside an ultrasonic bath working at a frequency of 40 kHz and a power of 70 W. The flask containing the target was filled with demineralised water and sealed; finally it was connected through a flexible hose to a glass beaker with water, in which an inverted graduated container was placed. The volume of the produced gas was determined directly by measuring the

displacement of the liquid. For each experiment the amount of ablated mass was determined using an analytical balance. Fig. 1a and b shows the experimental configuration used to produce hydrogen. The ablation time was kept constant at 5 min, corresponding to 3000 laser pulses, for all experiments. In order to characterize the produced gas, gas chromatography (GC) and Mass Spectrometry (MS) measurements were performed. 250 µL of gas obtained after the irradiation process were injected repeatedly and analyzed by gas chromatography (Gow-Mac 580 instrument) equipped with a molecular sieve 5 Å column at 35 °C, and an injector controlled by Clarity software V.7.0.01.402. Argon was used as carrier gas in the GC at 20 mL/min the effluent gases were monitored with a portable mass spectrometer (BELMass, MicrotracBEL Corp.).

## Results and discussion

When the target irradiation begins the appearance of bubbles produced at the target laser spot is immediately detected, independently of the presence of the ultrasonic field. Clearly, an increase in the number of bubbles is observed when the ultrasound is applied to the system. At the highest fluences after a couple of minutes the formation of a colloidal suspension is observable as expected due to the nanostructures production. As the irradiation time increases, this suspension avoids, because of absorption, that all the pulse energy reaches the target decreasing the ablation rate and consequently the production of bubbles.

### Gas identification

The gas produced under laser irradiation was analyzed by gas chromatography and mass spectrometry. For this purpose, samples were collected directly into glass vials of 10 ml and sealed with butyl rubber septa and cap. A gas-tight syringe was used to transfer 200 µL of the sample into the port of the gas chromatograph. Fig. 2 shows the chromatogram obtained after the injection at intervals of approximately 4.5 min of the five samples produced by laser irradiation: Mg, Al–Mg, Al, Si and Ti respectively. In all cases a very similar single peak at a retention time of 1.5 min corresponding to hydrogen was observed. No additional signals were detected by this

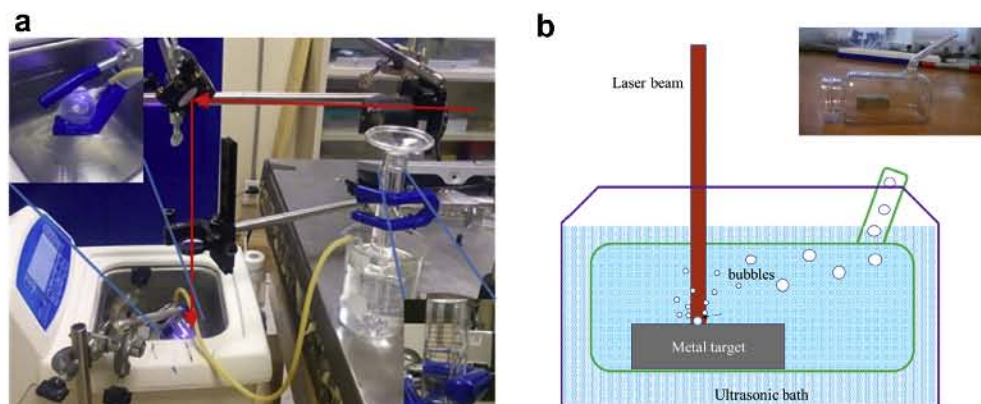
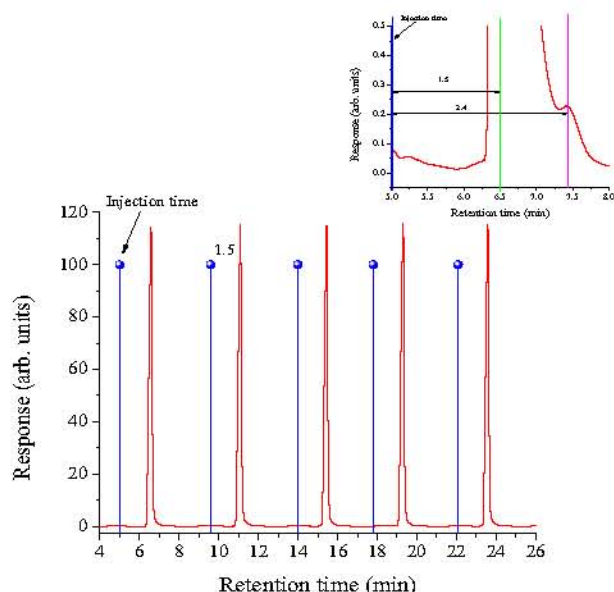


Fig. 1 a) Experimental setup for hydrogen production, b) detail of the glass flask containing the metal target.

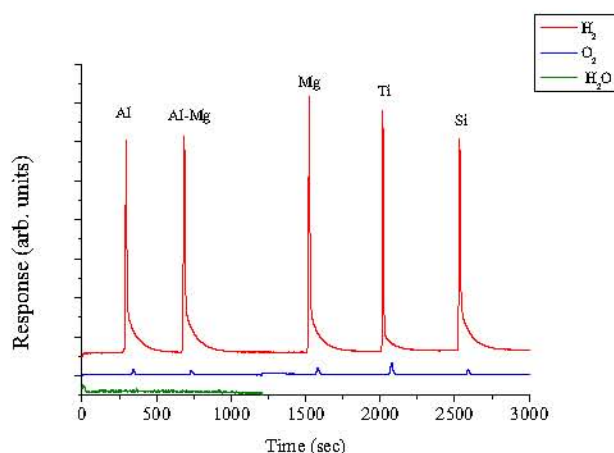




**Fig. 2** Gas chromatogram of five gas samples produced by laser irradiation of Mg, Al Mg, Al, Si and Ti targets respectively.

technique. In particular the signal due to oxygen, expected at a retention time of 2.4 min, appears with very low intensity as one can observe in the inset of Fig. 2. These results indicate that only hydrogen was produced independently of the irradiated metal. This result can be explained in terms of the high affinity of the employed metals to oxygen, forming oxides consequently allowing the release of pure hydrogen.

In order to complement the gas-chromatography results, the gas samples were analyzed by mass spectrometry. The signals coming from  $H_2$ ,  $O_2$  and  $H_2O$  were monitored since they are the most probable gases present in the samples. Fig. 3 shows the mass spectra of the analyzed samples. Strong signals due to  $H_2$  are observed confirming the results of chromatography above mentioned. Additional weak signals are observed revealing the presence of  $O_2$  with very low intensity. No signals due to water vapor ( $H_2O$ ) are observed. These



**Fig. 3** Mass spectra of the gas samples produced by laser irradiation of the different targets Al, Al Mg, Mg, Ti and Si.

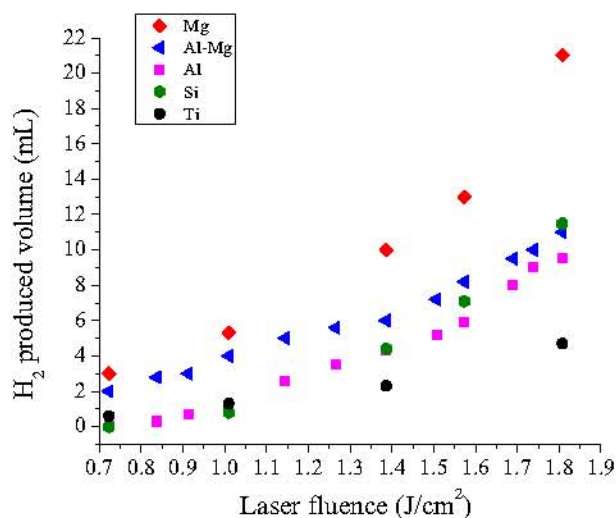
results show that the produced gas is composed mainly by molecular hydrogen with a low amount of molecular oxygen suggesting that this procedure allows the production of high purity molecular hydrogen.

### Hydrogen production

The hydrogen production from metals irradiation in presence of water due to metal-water reaction is shown in Fig. 4. All metals produced  $H_2$  when subjected to the simultaneous action of laser irradiation and ultrasonic field. It is seen that the  $H_2$  volume after 5 min of irradiation increases as the laser fluence increases from 0.7 to 1.8  $J/cm^2$ . For Mg and Si the data follow a non-linear monotonic behavior with similar tendencies whereas the Al Mg alloy, Al and Ti behave almost linear. Additionally, it is worth mentioning that hydrogen production increases linearly as a function of the irradiation time for all metals at the different laser fluences. These results can be attributed to an efficient removal of the oxide layer as well as to a higher temperature rise on the metal surface leading to a higher activation energy thus enhancing the metal-water reaction rate.

Titanium has the lower  $H_2$  production, from 0.6 to 4.7 ml in 5 min, this corresponds to production rates from 0.12 ml/min at the lowest fluence to 0.94 ml/min at the highest fluence. The higher  $H_2$  generation corresponds to magnesium, in this case, the produced volume varies from 3.0 to 21.0 ml in 5 min, with production rates from 0.6 ml/min at the lowest fluence to 4.2 ml/min at the highest fluence. In order to check the reproducibility of the results, at least three experiments were performed with each metal and for Al and Al Mg alloy seven additional laser fluences were used. The obtained results were in good agreement with the previous measurements.

It is worth mentioning that ultrasonic excitation alone does not lead to any gas production in the present experimental conditions, although it has been reported that the use of ultrasonic excitation allows splitting of water [34]. The



**Fig. 4**  $H_2$  volume as a function of the laser fluence used to irradiate the different metal targets in presence of ultrasound. All measurements correspond to the hydrogen volume obtained after 5 min of laser irradiation.

obtained results suggest a synergetic effect in which the removal of superficial layers by laser ablation is enhanced by the simultaneous cleaning of the surface by the ultrasonic field applied.

Fig. 5 shows the metal ablated mass during the  $H_2$  production experiment as a function of the laser fluence. As it is expected, a monotonically increasing behavior is observed. The relevant point here is that the amount of ablated mass is very low, ranging from the lowest value of 0.4 mg for Ti, to the highest value of 9.6 mg for Mg. This is the amount of each metal required to produce from 0.6 to 21.0 ml of  $H_2$  in 5 min respectively. As it is seen, Mg is ablated more easily followed by the Al–Mg alloy, then Al whereas Ti is hardly ablated. From the previous results Mg produces the highest volume of  $H_2$ , however, it consumes the higher amount of metal.

Fig. 6 shows the dependence of the  $H_2$  production per unit mass on the metal ablated mass. It is seen that for Ti the ablated masses vary from 0.4 to 1.3 mg correspondingly producing from 300 to 723 ml/min/gr of  $H_2$ . In the case of Al, the ablated masses vary from 0.6 to 1.4 mg producing from 23 to 1357 ml/min/gr of  $H_2$ . This result indicates that with the experimental configuration proposed Al is the most efficient metal for hydrogen production reaching values comparable and even higher than previous data reported using physical or chemical routes [9,10,35–37]. For Mg and the Al–Mg alloy the  $H_2$  production increases at a lower rate as the ablated mass increases. This can be in part attributed to the higher amount of ablated material dispersed in the water, forming a colloidal suspension, that blocks partially the laser beam thus diminishing the amount of energy incident onto the target and consequently the removed layer.

The obtained results can be explained in terms of displacement reactions, in which hydrogen is displaced by the metal from water forming hydroxides or oxides releasing  $H_2$  according to the following reactions:

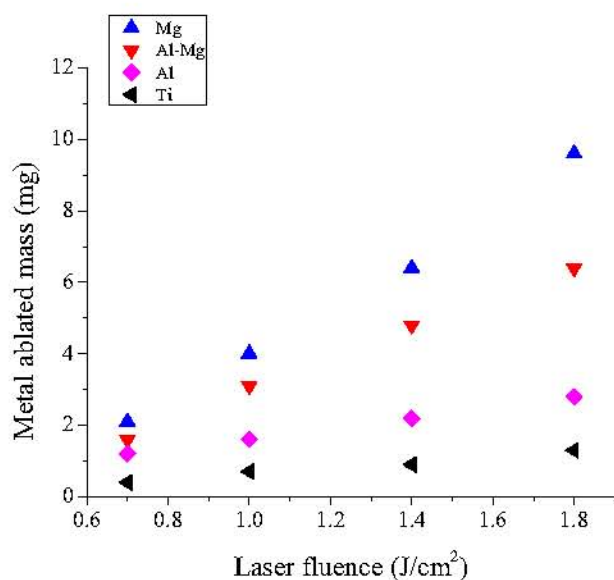


Fig. 5 Amount of ablated mass for Al, Al–Mg, Al and Ti as a function of the laser fluence used to irradiate the target after 5 min.

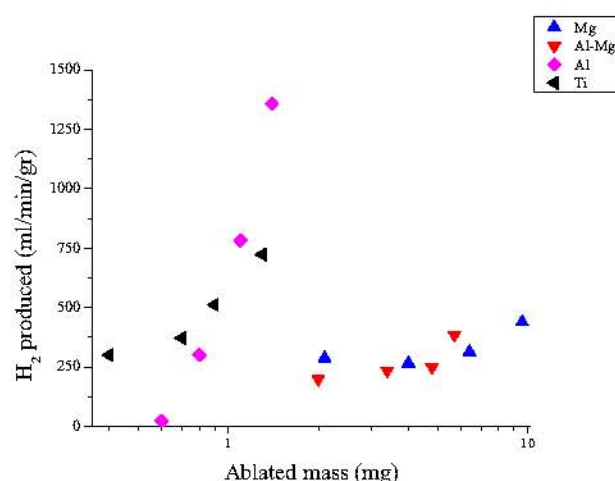
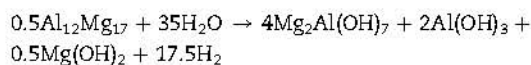
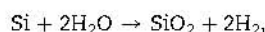
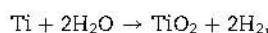
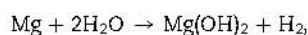
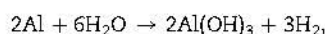


Fig. 6  $H_2$  production as a function of the metal ablated mass of the different metal targets after 5 min of laser irradiation.



In order to promote these reactions, the oxide surface layer must be removed to favor the contact of the pure metal with water. The thicknesses of such passivating layers have been reported elsewhere as: from 2 to 5 nm for Al [38], 2.6 nm for Mg [39], 1.5 nm for Si [40], 2.3 nm for Ti [41] and 4 nm for the Al–Mg alloy [42]. In general terms it is accepted that for laser ablation of metals, the incident laser radiation is absorbed by the conduction electrons in the metal. The absorbed energy is transferred to the lattice heating the solid to the melting point and then to the vaporization temperature leading to evaporation of the material [21,43]. Assuming that the laser beam can just be considered as a heat source which induces a temperature rise on the surface and within the bulk of the material, the reached temperatures should be at least the boiling point of each metal, that is, 2793 K for Al, 3553 K for Si, 3560 K for Ti, 1363 K for Mg and greater than 730 K (melting temperature) for the Al–Mg alloy. Therefore, the hydrogen production depends on the efficiency to remove the oxide layer and expose the metal to water. From the results presented in Fig. 5, the mean thickness of ablated layer for each metal and the number of laser pulses to remove such layer were determined, the results are shown in Table 1. It is clearly seen that more laser pulses are required to remove the native oxide layer from the titanium target followed by Al, the Al–Mg alloy, and for Mg less pulses are needed. These results agree well with the  $H_2$  production (see Fig. 4) indicating that it is



**Table 1** Ablation rates and number of pulses required to remove the native oxide layer at different fluences for the investigated targets.

F (J/cm <sup>2</sup> )	Al (nm/pulse)	Number of pulses	Mg (nm/pulse)	Number of pulses	Al Mg (nm/pulse)	Number of pulses	Ti (nm/pulse)	Number of pulses
0.7	0.53	9.4	1.43	1.8	1.05	3.8	0.10	23.0
1	0.70	7.1	2.74	0.9	2.05	1.9	0.18	12.7
1.4	0.97	5.1	4.38	0.6	3.17	1.2	0.23	10.0
1.8	1.23	4.0	6.57	0.4	4.23	0.9	0.34	6.7

crucial to remove the native oxide layer from the target. It must be pointed out that another important factor that influences the hydrogen production is the reaction between the nanostructures formed, as a result of the target ablation process, with water. It has been reported that nanoparticles of Si [44], TiO<sub>2</sub> [45], Al [46] and Mg [36] can act as catalysts to produce hydrogen. In this case the role of the ultrasound field is the activation of the highly reactive nanomaterials of the ablated metals to produce hydrogen. A deeper study to understand these combined processes is underway.

Additionally, it is worth mentioning that once the oxide surface layer is removed by laser irradiation, the chemical reaction of the metals with water continues but at a very slow rate. Particularly, the Al–Mg alloy requires approximately 19 h to produce the same H<sub>2</sub> volume that under continuous pulsed laser irradiation and ultrasonication requires 5 min. Therefore, this effect does not have an important influence in the presented results.

## Conclusions

The combination of laser ablation with an ultrasonic field for hydrogen production through reaction of water with some metal targets (Ti, Al, Mg and Al–Mg alloy and Si) was successfully implemented. It was found that aluminum appears to be the best option to produce hydrogen under the experimental conditions used in this work. The proposed procedure allows to extract hydrogen directly from water which is the most abundant source of this gas without environmentally harmful by-products emission. The gas chromatography and mass spectrometry techniques allowed the detection and identification of hydrogen as the main produced gas, with lower amounts of O<sub>2</sub>, thus indicating that hydrogen of high purity is obtained. An important advantage of the proposed H<sub>2</sub> production procedure is the low amount of mass consumed which leads to maximum production rates close to 1300 ml/min/gr of aluminum, comparable or even higher than previously reported values. Additionally, the proposed experiment produces nanomaterials in colloidal form that could be useful in other applications.

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