University of Crete

Bachelor thesis

Laser Induced Periodic Surface Structures on Nickel Electrodes for Hydrogen Production through Alkaline Electrolysis

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Contents

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Abstract

The following thesis was conducted in the Femtosecond Laser Spectroscopy in Solid State (FLASSS) laboratory of the Institute of Electronic Structure and Laser (IESL) of Foundation for Research and Technology– Hellas (FORTH) in collaboration with the Matter Structure and Laser Physics Laboratory of the Technical University of Crete. The purpose of this thesis is the fabrication of nanostructures on Nickel surfaces through irradiation by high fluence, ultrashort laser pulses, and the use of the nanostructured sheets as electrodes in alkaline electrolysis for Hydrogen production.

Scanning Electron Microscope was employed in order to assess the morphological characteristics of the obtained surfaces. We found that periodic surface nanostructures are formed by the laser irradiation. We performed a study of the different parameters that define the formation of the nanostructures, such as the polarization of the laser beam, the intensity and the scanning speed of the sample, or equivalently, the number of incident pulses per spot. The results showed that the periodicity is not affected by the scanning direction and also that there is no relation between the periodicity and the number of pulses irradiating a spot. The periodicity of the nanostructures is thus defined by the intrinsic properties of the material and the wavelength of the incident laser field.

The fabricated nanostructured electrodes were used in an electrolysis chamber for the evaluation of Hydrogen production. We found a significant enhancement of Hydrogen production when nanostructured electrodes are used. The results provide evidence that the electrodes irradiated with a larger number of pulses per spot are more beneficial to Hydrogen production. An enhancement factor of 3.7 with respect to the flat i.e. unstructured electrodes was found which is a remarkable improvement to the state of the art. The results are very encouraging for continuing studies in this direction employing different surface nanostructures, laser parameters and combinations of electrode materials.

1. Introduction

The usage of fossil fuels has had a great impact on the environment and is threatening to make irreversible changes. There has been an ever growing need to use friendly for the environment fuels. Renewable energy sources such as wind, photovoltaic and solar thermal power have been the main focus of attraction for energy production over the past years because of their non greenhouse gas emissions. Since these energy sources are intermittent, i.e. depending largely on weather conditions, there is a great demand for energy storage when the energy production is abundant so that it can later be used when the energy sources are not operable.

Hydrogen production through water electrolysis has a recent development over the last decades. More processes of Hydrogen production have been developed lately, other than the alkaline electrolysis, such as solid oxide electrolysis cells and proton exchange membrane cells. The reason behind this interest in Hydrogen is based on the fact that it is suitable to be used as an energy carrier to store electricity, when the production of energy from a renewable power source is excessive. In addition to that Hydrogen emits no greenhouse gases, and its energy density is about 3 times more than petroleum, making it more than suitable for both energy and environmental needs.

Water electrolysis is the procedure, in which direct current is applied to two electrodes that are submerged in water (liquid or vapor). In this way, the water molecules are decomposed to Hydrogen and Oxygen. As mentioned before, the usage of Hydrogen as a fuel is crucial both for industrial needs and for household everyday use. Hydrogen production is a field that can see more development, both in the new upcoming methods, as well as the alkaline electrolysis. The development that each method seeks, vary with the method used [1].

For alkaline electrolysis, progress in the electrodes used is sought. The research trends are focusing on the deactivation of Nickel, which happens during Hydrogen production. Hydrogen atoms form bonds with Nickel electrodes, changing Nickel's valence state and reducing its catalytic behavior. It has been proposed that coating Nickel electrodes with iron prevents the deactivation effect in long term. Additionally, creating slits and holes on the surfaces of the electrodes has been observed to have beneficial effects, by solving the so called "bubble effect". The bubble effect is a phenomenon which occurs during Hydrogen production and it is attributed to Hydrogen and Oxygen bubbles getting attached on the electrode's surface, preventing the electrolysis process. The methods used to affect the morphology of the surface of materials can be either chemical or the employment of lasers [2].

By irradiating the surface of materials with a high power laser beam, large amounts of energy are deposited on materials, triggering a variety of timescale-dependent physical processes, such as ablation, evaporation and phase explosion [3] [4] [5]. Such effects lead to removal and melting of the material modifying its surface. Reorganization of atoms forming cracks, defects, as well as periodic structures, can be observed due to such interaction depending on factors such as: the material that is being irradiated [6] [4] [7], the laser parameters, namely fluence, polarization, number of incident pulses and even the environment that the irradiation takes place in [3] [8] [9] [4] [5].

Using a high power, short pulsed laser beam, the creation of periodic structures on materials is controllable. The technique for forming periodic structures is known as Laser Induced Periodic Surface Structures (LIPSS) and such nanostructured materials receive an abundance of enhanced properties such as increased light absorbance, enhanced wetting properties and selective cell adhesion [3] [6] [8]. Such materials find use in a variety of applications because of their diffractive and super-hydrophobic behavior. Additionally, they are able to enhance the electric field created by electron concentration on the structures formed when electric current is applied to them, as well as obtain an increment in their surface area [8]. LIPPS is the product of the interference of the electromagnetic wave of the incident pulse with a surface electromagnetic wave, induced by the incident laser field [3] [4] [5] [6] [7] [9] [10]. The wave interference causes a periodic energy deposition, playing a significant role on the periodicity of the ripples that are formed.

The purpose of this work is the understanding of the role that certain laser parameters, like the number of incident pulses, laser's scanning direction and beam's polarization, play in the ripple formation, as well as the benefits that nanostructured electrodes have in alkaline electrolysis and Hydrogen production. We will discuss the procedure we followed for the construction of the electrodes that were later used and tested in the production of Hydrogen gas, as well as the promising results we received by comparing an untreated Nickel electrode to a nanostructed one, seeing a clear enhancement in Hydrogen production by a factor of 3.7 when using the nanostructured one. Thus, this work contributes to reducing the environmental footprint by engaging laser-nanostructuring in Hydrogen production through alkaline electrolysis.

2. Femtosecond laser-matter interaction

The fundamental theory of metal removal is based on laser irradiation and it's depended on the laser pulse width, since laser pulse duration determines the physical process of energy deposition on the target material. Since interactions between electrons and lattice take place in timescales of a few picoseconds and therefore during irradiation with a pulse that is a few nanoseconds long, there is enough time during irradiation for heat to be transferred from the excited electrons to the lattice through collisions and a thermodynamic equilibrium between the lattice and the electrons to occur. This leads to impacting a greater area and to several thermal defects being created on the material, making wide nanosecond pulses a non-optimal way to control and tailor the creation of such nanostructures. This is explained considering the heat transfer that leads the material to a melting point and subsequently to a vaporization point which ejects the molten material. Femtosecond laser ablation on the other hand, due to the ultra short pulse duration, is a non-thermal process. Electron-lattice interaction and thermal diffusion processes have typical durations much longer than the pulse duration and thus, thermal equilibrium between electrons and lattice in not achieved within the pulse duration. Such ultrashort pulses give the opportunity of minimizing the affected area and creating more precise structures on materials. Spallation, phase explosion, fragmentation and vaporization are the main phenomena that are triggered during femtosecond pulse irradiation [3] [4] [5] [8] [11] [12] [13]. In Fig.1 a timescale dependence of the physical processes that take place during laser and matter interaction for nanosecond and femtosecond pulse width is shown.

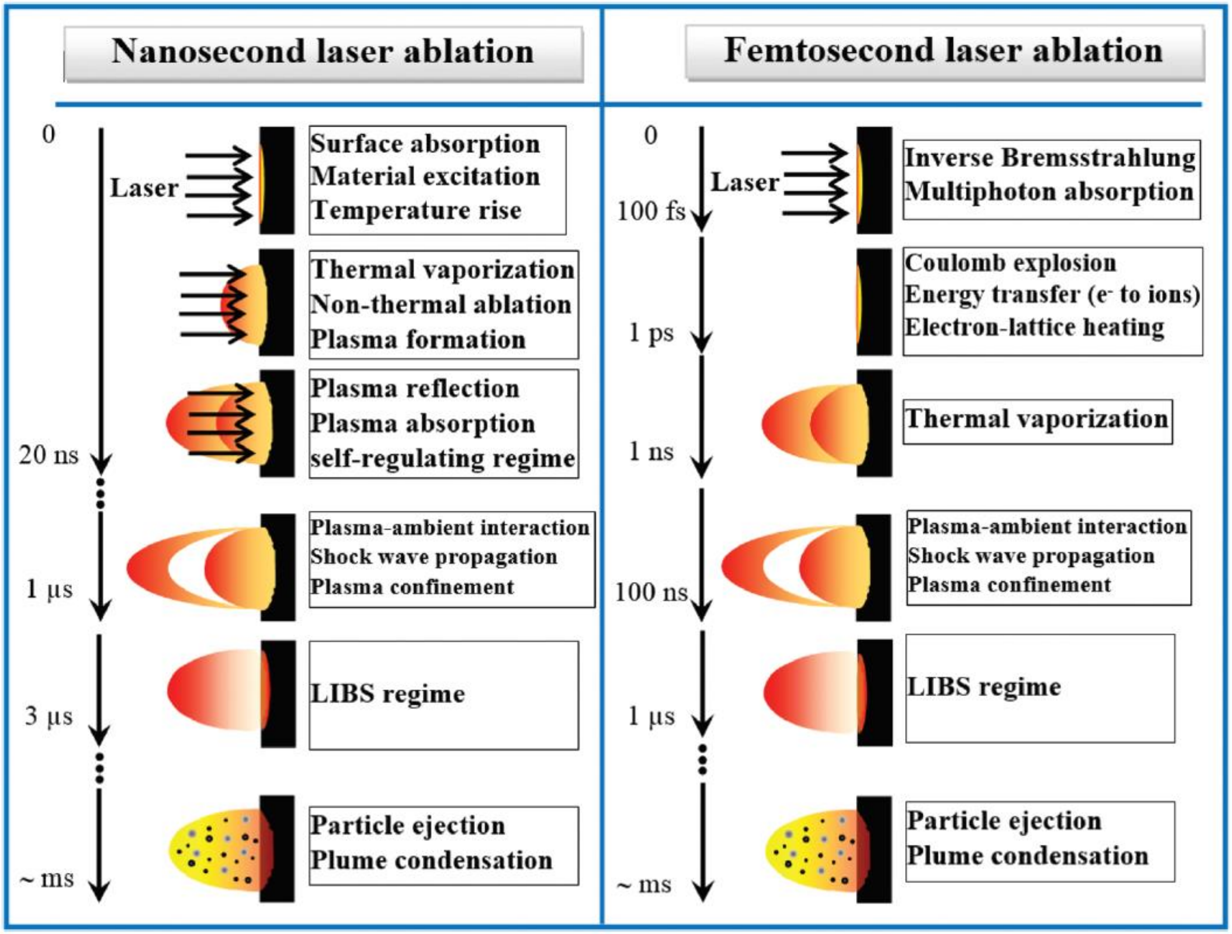

Figure 1: Approximate time scales of laser energy absorption and ablation, along with the various processes for nanosecond and femtosecond laser ablation in ambient gas [14].

The processes that take place during metal irradiation are further analyzed as follows. During laser-matter interaction, a portion of the laser energy is absorbed by the free electron system while the rest is reflected by the surface. Collisions between electrons cause their thermalization and therefore their temperature raise compared to the lattice temperature. Since ions cannot absorb optical radiation directly, because they cannot follow the fast oscillations of the electromagnetic field, the lattice of the metal is heated up through their collision with energetic electrons. The huge mass difference between ions and electrons means that only a small portion of energy can be transferred by each collision, leading to a slower heating process for the lattice compared to the electrons. The thermodynamic equilibrium between the electron system and the lattice is reached after multiple electron-phonon relaxation events and therefore the lattice temperature remains low during the whole process. The mechanism that governs the interaction between a femtosecond laser pulse and a metal is shown in Fig.2 [5].

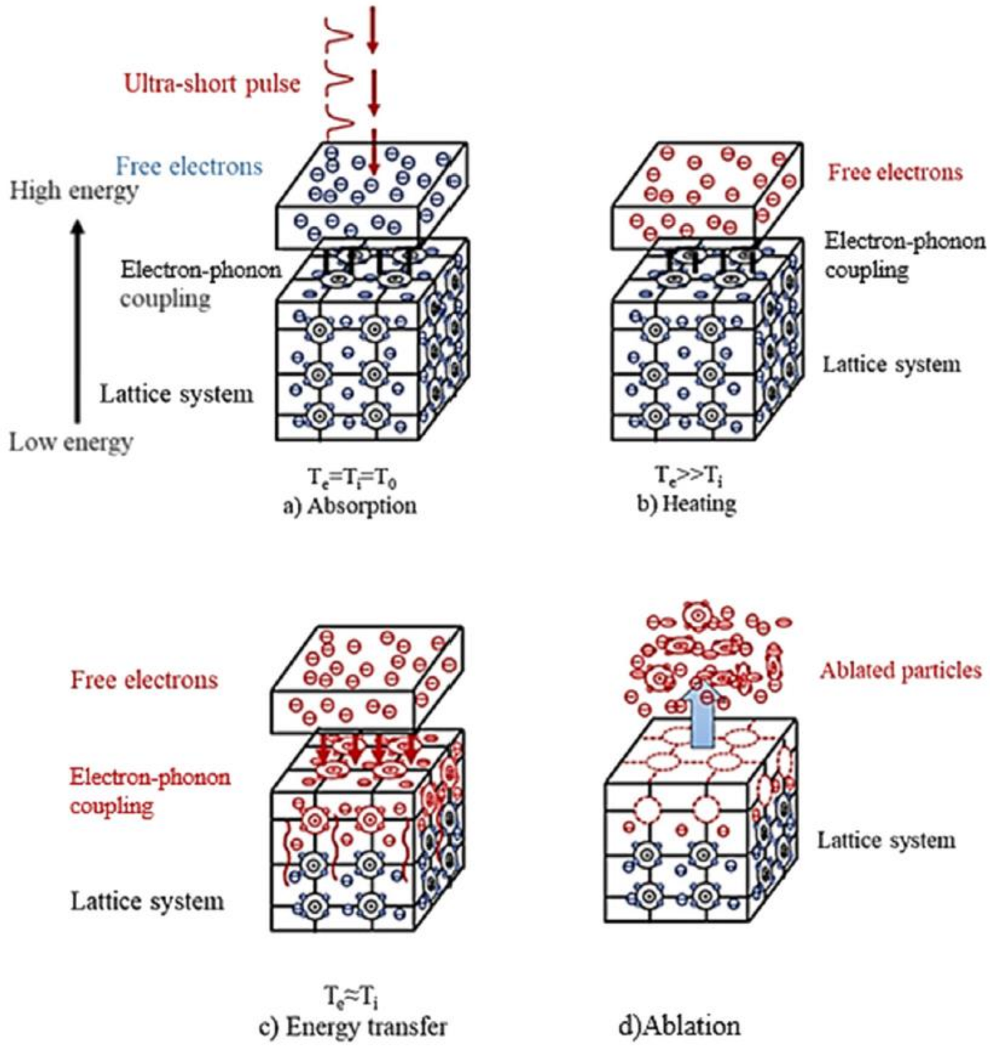

Figure 2: Schematic diagram of femtosecond pulse laser-matter interaction mechanism. T_e – electron temperature, T_i – lattice temperature, T_0 – ambient temperature [5].

The four ablation mechanisms that are suggested to play important roles are the following.

1. Spallation, which is the failure of the material to follow the creation of defects that are induced by tensile stresses, leading to the ejection of material of the top most layer of the solid. Femtosecond laser irradiation on materials changes both the volume and their pressure, which is the main reason behind this reaction.
2. Phase explosion, which occurs due to the fast heating and the phase transition that the laser pulses inflict on the surface of the material. Phase explosion happens when a liquid approaches the thermodynamical critical point temperature, at which point homogeneous nucleation takes place.
3. Fragmentation, that results in spatially non-uniform strain rates that are caused by the relaxation of large thermoelastic stress. Because of the non-uniform strain, the fluid initially turns into an ensemble of clusters leading to a structural reorganization of the solid.
4. Vaporization, which is the rapid decomposition of the solid following the absorption of energy that exceeds the cohesive energy of the material [3] [5] [11].

3. Laser Induced Periodic Surface Structures

LIPSS has a history of four decades, but recently it has received more attention over the beneficial effects structured materials give, as well as the advancements in laser technology. The formation of LIPSS is based on the melting and resolidification of the surfaces of materials in a periodic manner. The formation of the periodic structures is the result of the interference pattern of the pulse with an induced-by-the-pulse electromagnetic field. Irradiating a metal with a laser beam causes a surface electromagnetic wave to rise, due to the oscillations of the electrons. The electrons oscillate in the direction of the pulse's polarization. The interference pattern that is created is limited to the polarization axis and thus a periodic pattern of alternating bright and dark stripes is created. Thus, the deposition of energy attains a periodic distribution. Fig.3 shows a schematic of the induced-by-the-pulse electromagnetic field that is created on the surface of the material during irradiation.

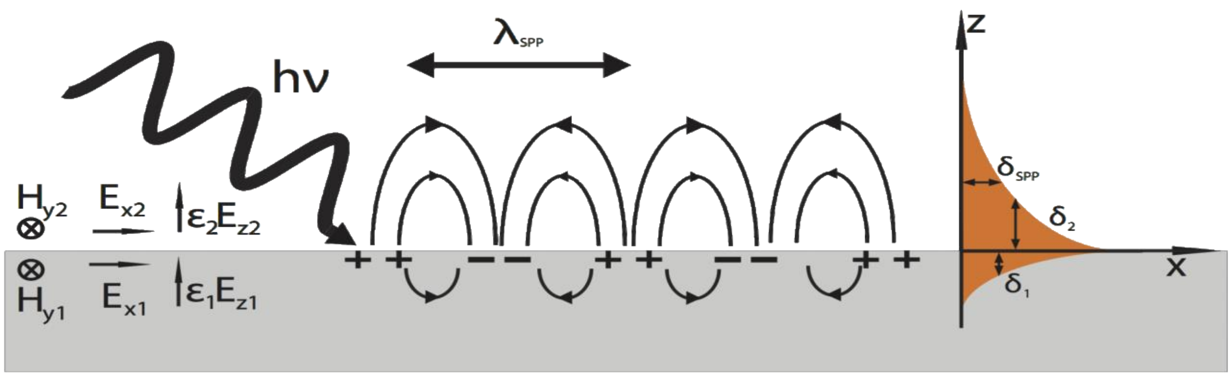

Figure 3: Schematic representation of the excitation of a surface wave on the material's surface by an incident laser field [15].

Energy is deposited periodically according to the interference pattern, which leads to a periodic temperature rise on the material. As the temperature rises, at the energy deposited areas, the material reaches about 0.907 its critical temperature, the temperature in which liquid, solid and vapor phase can occur at the same time, which leads to a phase transition from solid to liquid. The molten matter gets depressed due to the resulting reduction of the surface tension. A rise occurs at the peripheral of the laser beam due to recoil pressure pushing the molten material away in a radial direction because of the phase transition [3] [4] [11]. During the cooling process of the area, the surface resolidifies after sufficient time (in the order of many nanoseconds) creating the observed periodic nanostructures. There is a relation between the plasmon wavelength and the wavelength of the pulse as well as the dielectric permittivity of the material used, which is given by the following expression:

$$\lambda_s = \lambda\sqrt{\frac{\varepsilon' + \varepsilon_d}{\varepsilon' \varepsilon_d}}$$

Where λ_s is the Plasmon's wavelength, $\lambda$is the wavelength of the laser field, $\varepsilon'$is the dielectric permittivity of the material being irradiated and ε_d is the dielectric constant of air[3] [4] [8] [11].Hence, laser's wavelength his responsible for the periodicity of the structures formed, while laser's polarization is affecting the orientation.

Depending on the material that is being irradiated, there have been two main categories, concerning the periodicity of the structures that are distinguished using this technique. For strong absorbing materials, like metals and semiconductors, low-spatial-frequency LIPSS (LSFL) are observed with a period close to or a little smaller than the irradiation wavelength and an orientation perpendicular to the laser beam polarization. In dielectrics, the orientation has been observed to be either perpendicular or parallel to the beam polarization, with a period either close to the wavelength used, or close to λ/n, where n represents the refractive index of the dielectric material. For metals and semiconductors there have been observations of LIPSS periodicity ranging from 600 nm to 800 nm, using a laser wavelength of about 800 nm, depending on the fluence and surface roughness [3] [6] [7]. On the other hand, for transparent materials, there has been observed high-spatial-frequency LIPSS (HSFL), with a periodicity significantly smaller than the irradiation wavelength and with orientations either perpendicular or parallel to the polarization [5] [8] [9]. There have been observations of LIPSS periodicity on Nickel at 600-650 nm for LSFL and 160-350 nm for HSFL [16] [17].

As mentioned earlier both semiconductors and metals have similar behavior in nanostructure formation when irradiated by a short pulse, high energy laser beam. When a semiconductor is heated it creates pairs of holes and electrons, creating a high density of electrons and therefore behaving like a metal. When irradiated by a laser beam, semiconductors are expected to have a similar response to the incident pulses as a metal and create plasmon waves to interfere with the incident pulses following the same creation process that was mentioned.

4. Hydrogen Production Through Alkaline Electrolysis

Alkaline electrolysis is the most mature method of Hydrogen production. An alkaline electrolysis cell consists of two electrodes that are submerged in a liquid mixture of water and an electrolyte, and separated with a semipermeable membrane as shown in Fig.4. During this reaction water plays the role of the sole reactant, meaning that with the proper supply of water, electrolyte concentration can be held steady. A direct current is applied and electrons flow towards the cathode, where they are consumed by Hydrogen cations to form Hydrogen. In order to keep the electrical charge in balance, hydroxide anions transfer through the electrolyte solution, where the hydroxide anions give away electrons that return to the positive terminal of the power source [1] [2]. Fig.4 shows an alkaline electrolysis cell, as well as the chemical reactions that take place.

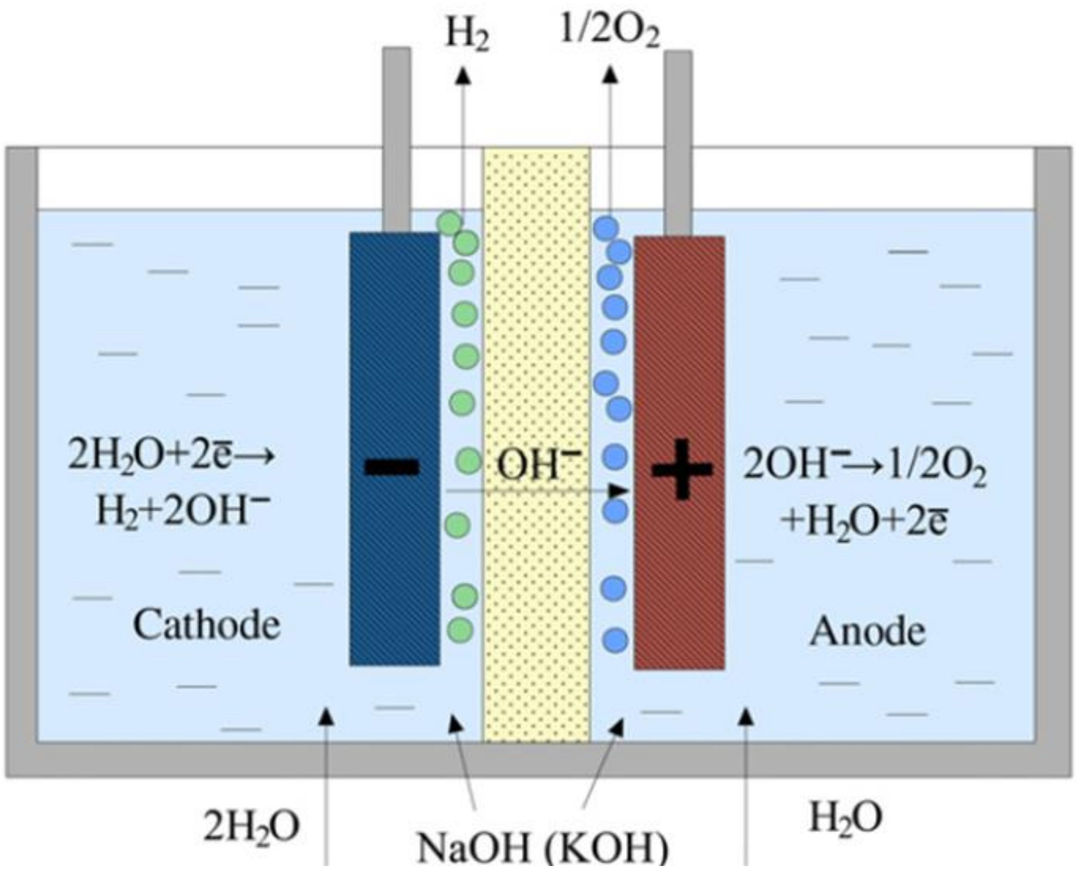

Figure 4: Schematic diagram of an alkaline electrolysis cell [1].

The chemical reactions that occur in an alkaline electrolysis cell are the following:

$$Cathode: 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$

$$Anode: 4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

$$Overall: \; 2H_2O \rightarrow 2H_2 + O_2$$

Hydrogen production using alkaline water electrolysis main advantages are:

- The capital expenses are relatively low due to cheap cell materials.
- Water can be fed directly in the process without the need of purification.
- It is a proven technology with well-established operational costs.
- The lifetime of an alkaline electrolysis system is satisfactory for continuous operation.

On the other hand, alkaline electrolysis is met with a few drawbacks, with some of them being:

- Alkaline electrolysis cells operate at very low current densities (due to limitations imposed by the bubble effect).
- Asbestos, which used to be the most used material as a diaphragm, is being replaced due to its toxicity.
- The quality of the Hydrogen produced comes with impurities of Oxygen and water vapor with alkali [1].

Hydrogen production has received a great deal of attention and more techniques for Hydrogen production have been developed over the last decades. Namely, Proton Exchange Membrane (PEM) cells, which shows promising results in the Hydrogen production, but with considerably high capital expenses needed to create the cell and maintain the production of Hydrogen since the water used need to be purified, and Solid Oxide Electrolysis (SOE) cells, which works at high temperatures, meaning that less electrical energy is needed for it to operate because of the improved thermodynamic conditions that are achieved, but there are some safety issues that are still need to be addressed for the usage of this technique. Table1 shows a comparison in the efficiency and maturity of the different methods of water electrolysis that were mentioned.

Technology	Efficiency	Maturity
Alkaline Water Electrolysis	59-70%	Commercial
Proton Exchange Membrane	65-82%	Near term
Solid Oxide Electrolysis	40-60%	Mediate term

Table 1: Comparison of the electrolysis methods [2].

Due to the well established technology and its popularity, further development in alkaline electrolysis will give more promising results in the Hydrogen production technology. The maturity of this method allows quick implementations of further improvements and therefore it is more promising in promoting Hydrogen fuel in the market.

5. Nanostructured Electrodes for Alkaline Electrolysis

Nickel is the dominant metal that's been used as an electrode for alkaline electrolysis because of its stability and activity. Recent researches suggest that modifying the surface of the electrodes will help the escape of gas bubbles that partially cover the surface of the electrodes that take place during the process of water electrolysis and is one of the main reasons alkaline water electrolysis cells operate at low current densities. Oxygen and Hydrogen gas bubbles are formed on the surfaces of the anode and cathode, preventing water flow to those areas and, therefore, limit the reaction. Those bubbles get detached from the surface only when they grow big enough. It's been addressed that modifying the surfaces with slits or holes, facilitates the escape of gas bubbles that are forming [2] [18] [19] [20].

A way to boost the Hydrogen production efficiency is by reducing the electrical resistances that exist in the system. The electrical resistances are what cause heat generation which leads to the wastage of electrical energy. The electrical resistances have three main components:

1. The resistances in the system circuits, which are determined by the types and dimensions of the materials.
2. The mass transport phenomena including the ions transfer in the electrolyte, depending on the electrolyte concentration and separation distance between the anodes and cathodes and the diaphragm between the electrodes.
3. The gas bubbles covering the electrodes and the diaphragm, which occurs by the presence of bubbles forming in the electrolyte solution and on the electrode surfaces, causing additional resistances to the ionic transfer and surface electrochemical reactions.

By using nanostructured electrodes, we get an improvement in the surface area used and consequently enhance the Hydrogen production since due to having more area for the reaction to take place at. Additionally it is expected that ripples facilitate the escape of the bubbles formed by Hydrogen and Oxygen gas that get trapped on the surface, leading to a better flow of water. The improvements that nanostructured electrodes promise are higher current density to be applied to the electrodes, since the current density used is limited to 1000-3000 Am^{-2} for a typical alkaline water electrolysis cell.

6. Experimental setup

We used a Ti:Sapphire laser amplifier system with a minimum pulse duration of 30 fs and a Repetition Rate of 1kHz. The central wavelength was at 795nmand the maximum energy per pulse was 0.8mJ.The laser amplifier is pumped by a diode-pumped Nd:YLF laser. It is also seeded by a Ti:Sapphire oscillator which is optically pumped by a $Nd:YVO_4$ laser. The oscillator pulses were temporally stretched by propagating through optical glass, prior to amplification. The stretched pulses passed through the Ti:Sapphire crystal for amplification to pulse energy up to ~0.8 mJ with a bandwidth of ~ 40 nm. A prism compressor would then compress the pulses to a minimum pulse duration of 30 fs. At the laser processing workstation (Fig. 5) a Michelson-type interferometer (set up for experiments involving spatiotemporal combination of two laser beams, not used in the experiments described here) splits the beam in two equal parts. One of them is dumped and the other one is guided to a periscope mirror setup which was used to raise the beam and irradiate the samples in a vertical manner. With a plano-convex lens with a focal length of 200mmthe beam was focused on the Nickel samples that were positioned on a moveable stand. With the use of programmable motors, precise irradiation could be achieved on the entire surface of the samples used. A schematic of the experimental laser setup used to irradiate the Nickel samples is shown in Fig.5.

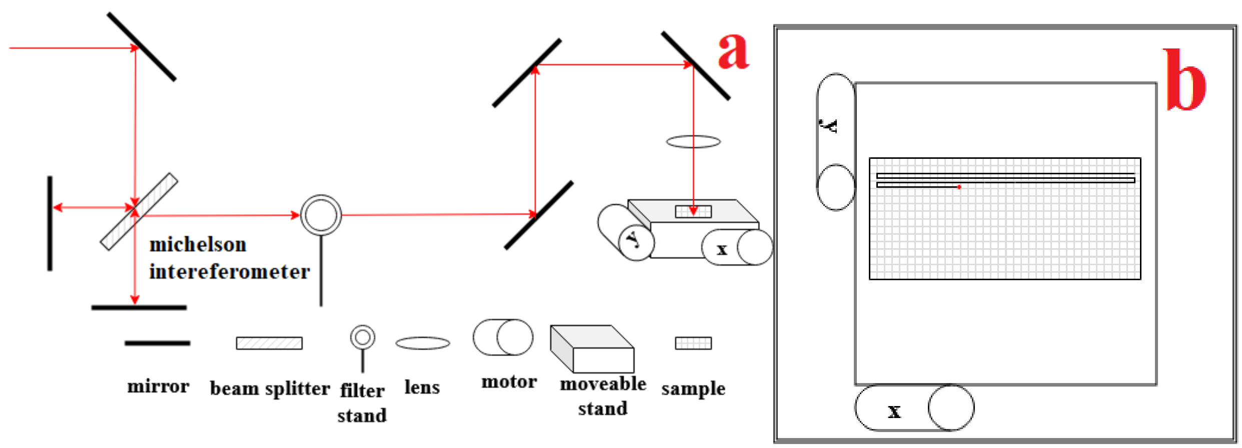

Figure 5: a) Schematic of the experimental setup used for nanostructuring the Nickel samples, **b)** view of the sample during the irradiation process.

The estimated pulse duration that reached the sample is estimated to be 100 fs. Due to the broadband (~ 40 nm) nature of the laser pulses propagation through optical devices like lenses lead to chromatic aberrations and pulse widening, since the lens interacts in a different manner with different frequencies leading to intense spatial and temporal dispersion, and. consequently, pulse width broadening to an estimated ~ 100 fs.

7. Experimental Results and Discussion

7.1 LIPSS on Nickel samples

Following the irradiation of Nickel samples and the morphological modification of their surface, we used a Scanning Electron Microscope (SEM) in order to acquire high resolution images of the irradiated areas. The images acquired were used as data to study the resulting surface structures, by analyzing them with two-dimensional Fourier Transform (2DFFT). 2DFFT achieves a translation of the spatial coordinates that are provided by the image acquired into inverse space (spatial frequency).

We performed a parametric study on the influence of the laser scanning direction and the number of incident pulses per spot had on the resulting structures. The resulting structures are shown in Fig.6.

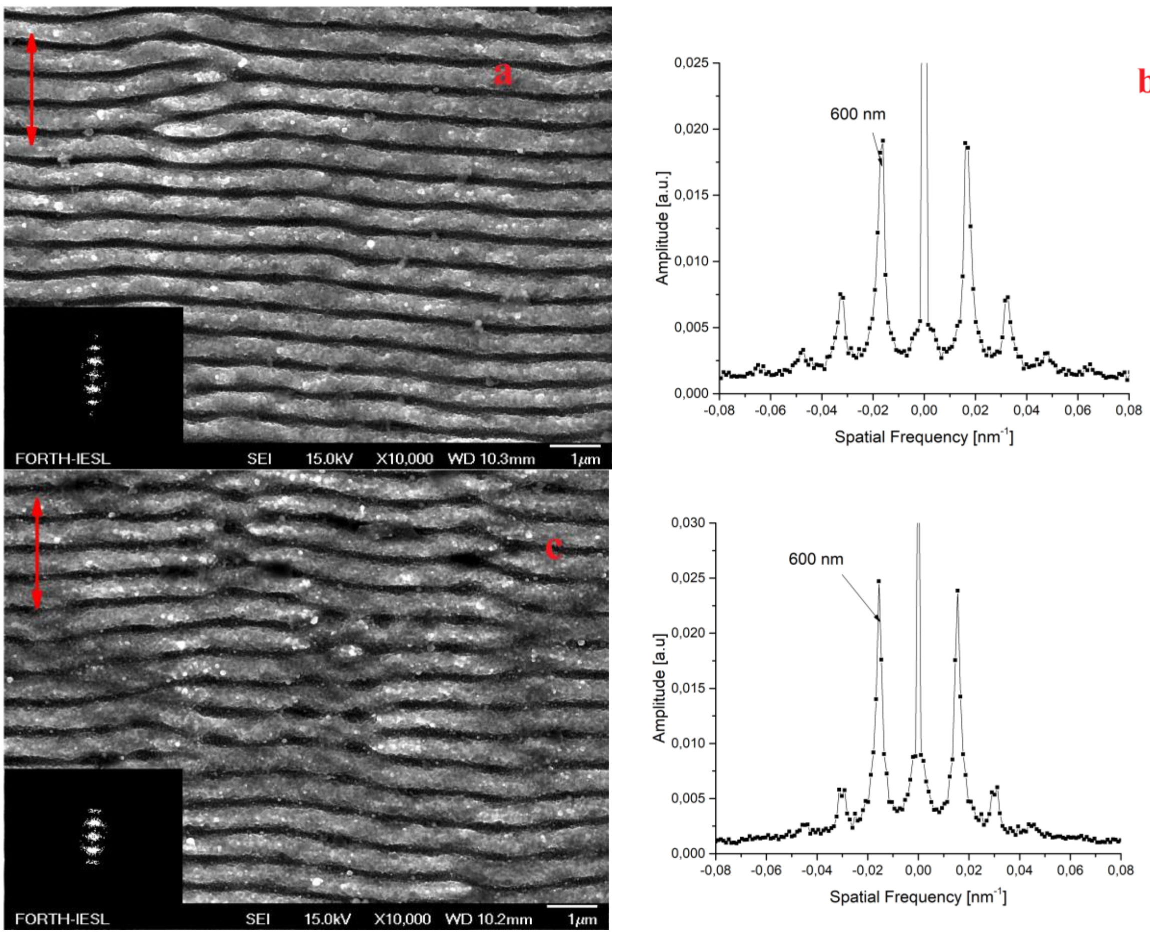

Figure 6: a) Nickel sample irradiated with 45 pulses per spot at a fluence of φ_0=2.0±0.1Jcm^{-2} and a beam radius-1/e^{2}of ω_0=9.2±0.3 μm irradiated parallel to the polarization, **b)** 2DFFTgraph of a, **c)** Nickel sample irradiated with 45 pulses per spot at a fluence of φ_0=2.0±0.1Jcm^{-2} and a beam radius-1/e^{2}of ω_0=9.2±0.3 μm irradiated perpendicular to the polarization and **d)** 2DFFT graph of c.

Scanning direction	Primary Beam	Secondary Beam	Number of incident pulses per spot	Fluence
Perpendicular to polarization	600±20 nm	580±20 nm	45	2.0±0.1 Jcm^{-2}
Parallel to polarization	600±30 nm	590±20 nm		
Perpendicular to polarization	595±8 nm	580±10 nm	96	
Parallel to polarization	620±3 nm	590±10 nm		
Perpendicular to polarization	470±50nm	450±60 nm	290	
Parallel to polarization	580±130 nm	540±60 nm		
Perpendicular to polarization	600±20 nm	580±10 nm	48	2.1±0.1 Jcm^{-2}
Parallel to polarization	620±4 nm	590±20 nm		

Table 2: periodicity results produced by 2DFFT performed on a Nickel sample. The red values are obtained from surfaces that exhibited low contrast giving very broad peaks in the 2DFFT analysis.

The results that 2DFFT analysis produced are shown in Table2. Within the data dispersion, we show that the scanning speed does not affect the periodicity of the structures formed. Researches show that HSFL can be achieved with a high number of pulses and therefore the number of pulses play a role in the morphology of the structures formed [17]. Fig.7 shows the relation between the number of incident pulses per spot and the periodicity of the formed structures. We observe that given the relatively high dispersion (Fig.8) of some of the data points the general trend shows that the periodicity of the LIPSS is not affected by the number of pulses per spot, although a suspicion of a downward trend could be noticed.

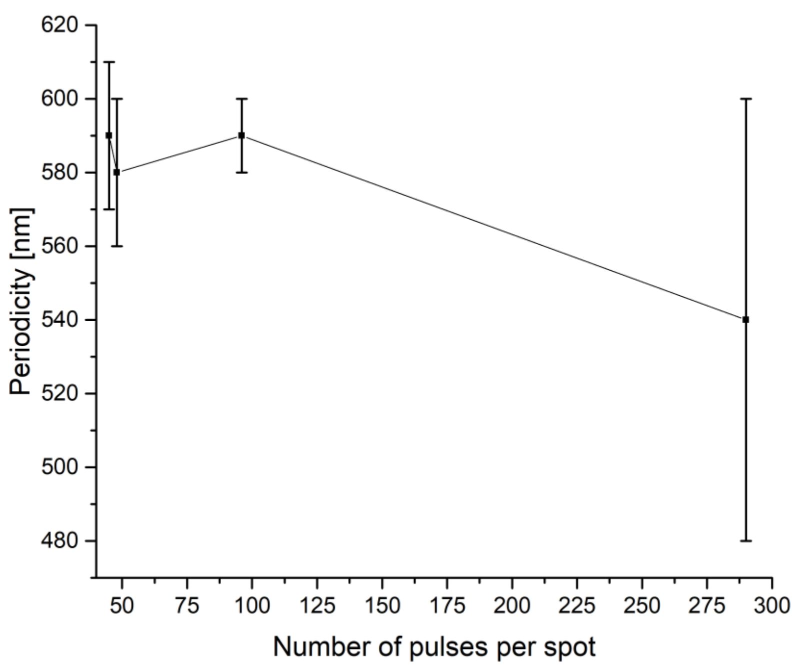

Figure 7: Dependency of the periodicity of LIPSS formed on Nickel samples, to the number of incident pulses per spot.

In [Fig.8](#) the obtained nanostructures that exhibit low contrast thus resulting in very broad characteristic peaks in the 2DFFT analysis are shown.

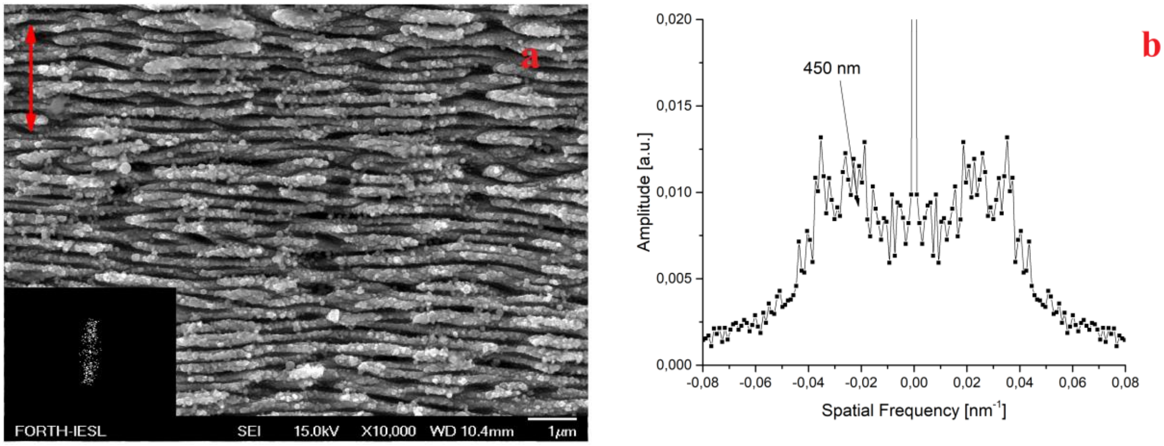

Figure 8:a) Formed structures when irradiated with 290 pulses per spot, **b)**graph of 2DFFT analysis.

As an effort to explore the possibility to irradiate larger material surface and therefore create LIPSS faster and more efficiently we examined the effect of a loosely focused laser beam. For this, we shifted the position of the lens in order to broaden the beam spot from 9.2±0.3 μm to 49±1 μm at $1/e^2$ beam radius. This resulted to fabrication of periodic nanostructures with a significantly broader periodicity distribution as can be seen by the width of the corresponding Fourier peaks in Fig.9. A comparison of the structures created with strongly focused vs. loosely focused laser beam is shown in Fig.9.

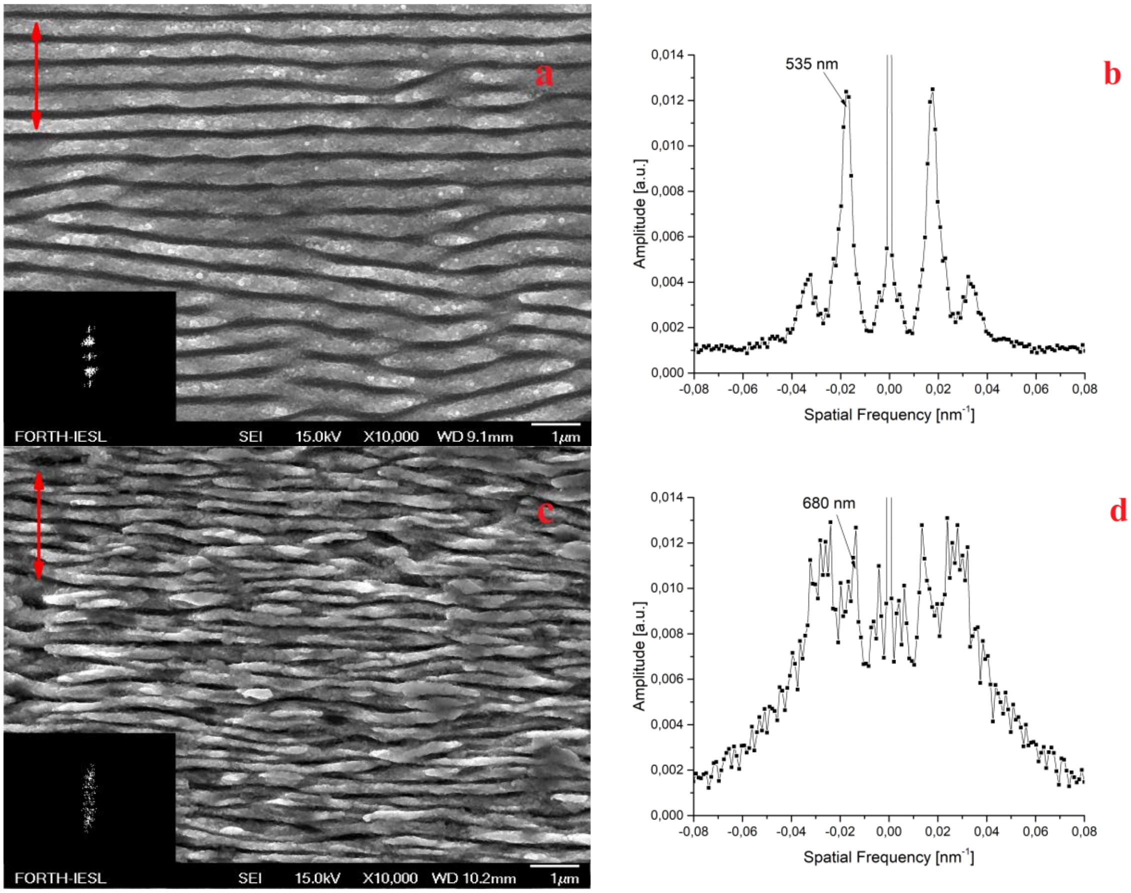

Figure 9: a) Nickel sample irradiated with the beam focused on the sample, **b)** 2DFFT graph of sample a, **c)** Nickel sample irradiated with the beam's focus shifted at 1cm and **d)** 2DFFT graph of sample c.

The parametric research that was conducted in the morphology changes that ultrashort pulses have on Nickel, show that the scanning direction does not affect the periodicity of the formed structures. In addition there were no morphology changes in the periodicity of the formed structures in the range of 45 to 96 incident pulses per spot. The data we acquired for 290 incident pulses per spot show a lower periodicity on the structures formed, but the results that were obtained exhibit a broad periodic distribution, leading us to the assumption that the periodicity remains steady (Fig.7). The experimental results of the LIPSS formed show a periodicity of about 600±20 nm. The plasmon wavelength is calculated to be 764 nm [21]. The discrepancy is attributed to the fact that the Nickel samples that were irradiated were smoothened with the use of mechanical means which may result is strong variations of absorbance throughout the surface. Further the samples used are polycrystalline while the theoretical value corresponds to single crystal. Nonetheless the resulting periodicity is in accordance with previously published experimental work [16]. A more detailed research would be more determining of the role the number of pulses have in the LIPSS formation. In addition to the number of pulses the impact of the fluence should also be examined further, so as to receive information on the resulting structures at different fluences.

7.2 Hydrogen production

The nanostructured Nickel samples were subsequently tested for their functionality as electrolysis electrodes. These measurements have been performed in the Matter Structure and Laser Physics Laboratory of the Technical University of Crete. The setup used for the Hydrogen production experiments is shown in Fig.10. Two cylindrical chambers were filled with the water electrolyte (K) solution. Plexiglass endings were used to control the distance between the anode and cathode and a Zinfon Perl membrane for Hydrogen and Oxygen separation. Electrolysis was performed at steady potential of 3 V. Nanostructured electrodes were used as anode and flat, i.e. not irradiated Nickel electrodes, as cathodes. The Hydrogen and Oxygen gas was gathered through tubes and measured with displacement of the electrolyte through semipermeable membranes.

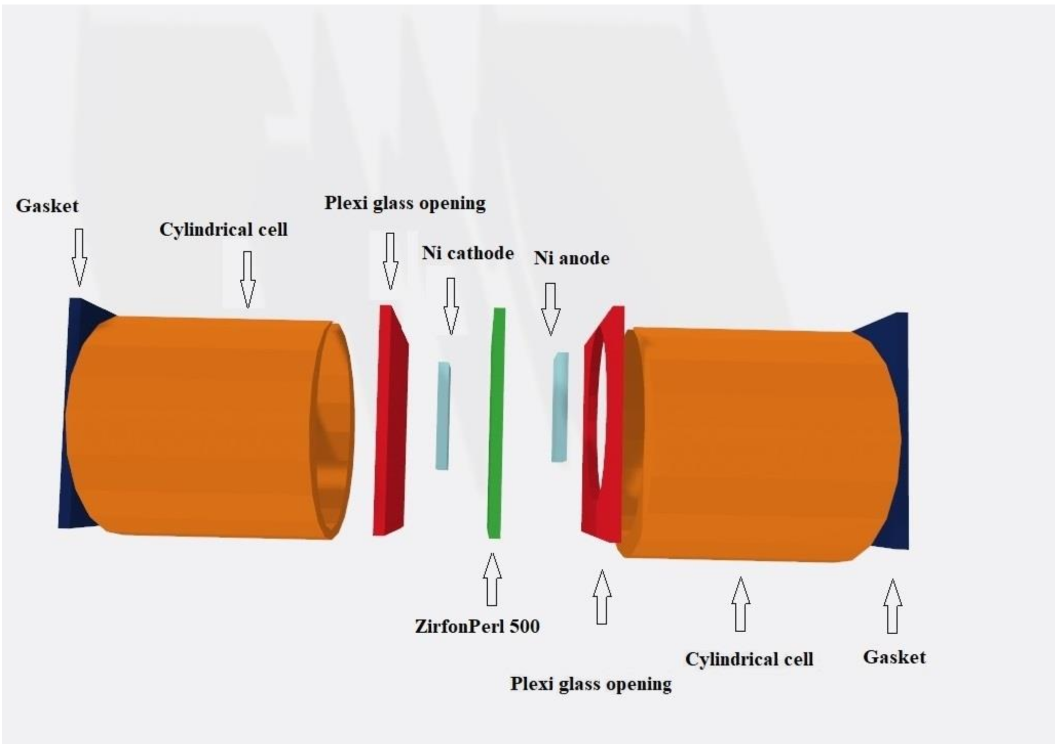

Figure 10: Schematic diagram of the electrolysis cell used.

A comparison of the Hydrogen produced between some of the nanostructured electrodes that were used for the electrolysis experiments are showed in Fig.11.

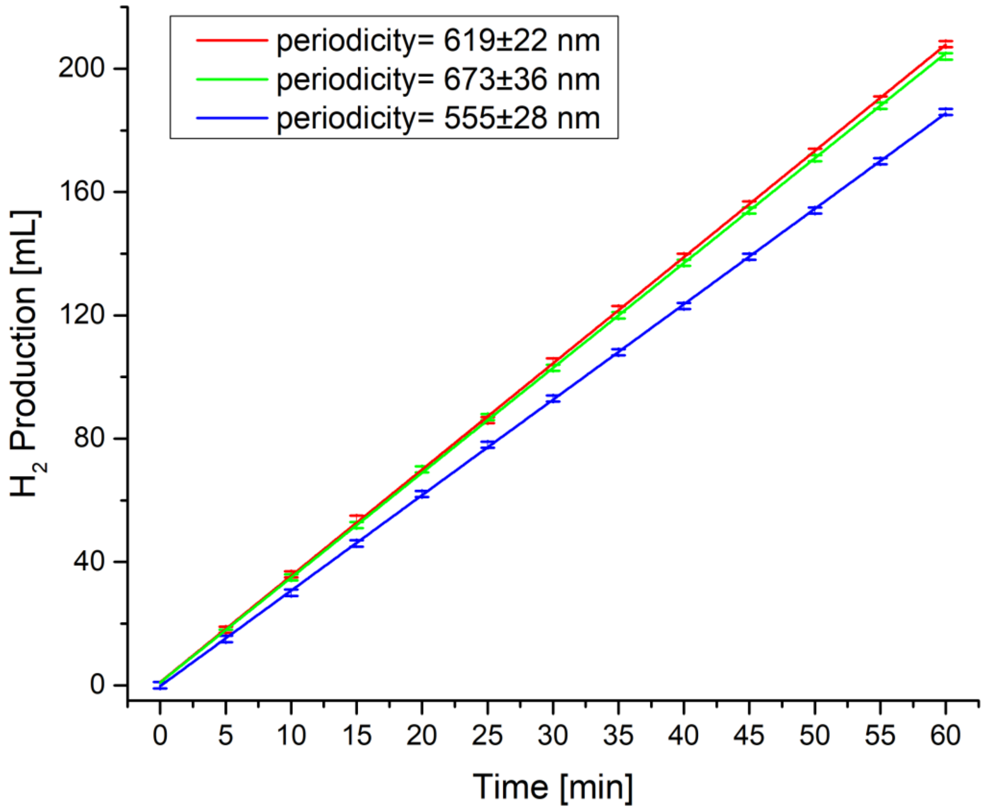

Figure 11: Hydrogen produced using nanostructured electrodes.

As shown in Fig.11 electrodes with higher periodicity produce more Hydrogen in the span of an hour. By nanostructuring the electrodes with periodic nanostructures, we essentially enhance their effective surface area, thus creating more surface for the reaction of electrolysis to take place. For that reason, lower periodicity leads to higher effective surface area, since more LIPSS are formed. In Fig.11 we observe the exact opposite to our expectation, i.e. the electrodes with higher periodicity (larger LIPSS period), and therefore an expected lower effective surface area, show a small but noticeable enhancement in the Hydrogen production compared to low periodicity nanostructured electrodes. When looking at Fig.9 we see that the low contrast LIPSS of Fig.9c exhibit a broad periodicity distribution while on the other hand the high contrast LIPSS of Fig.9a exhibit a very sharp and narrow periodicity distribution as can be seen at their corresponding Fourier analyses. The broad periodicity distribution can very well result to an effective surface area that may exceed the effective area of the high contrast nanostructures of Fig.9a. This needs further investigation with Atomic Force Microscopy analysis and/or tilted or cross sectional SEM analysis which was not available in this work but it is in our experimental plans in the immediate future. Further, when having a closer look at the LIPSS of Fig.9 one can notice secondary nanostructure formation in the form of nanoparticle flakes and other even smaller nanostructures dispersed all over the LIPSS area and they have a very broad size and shape distribution. These small nanoparticles may very well enhance the electric field locally, which in turn further enhances the electrolysis reaction and therefore it is expected to increase the Hydrogen production efficiency. Again, further experimental studied are needed to consolidate these hypotheses.

A comparison in Hydrogen production of the nanostructured Nickel electrode, with the highest efficiency achieved, with a pure Nickel electrode is shown in Fig.12.

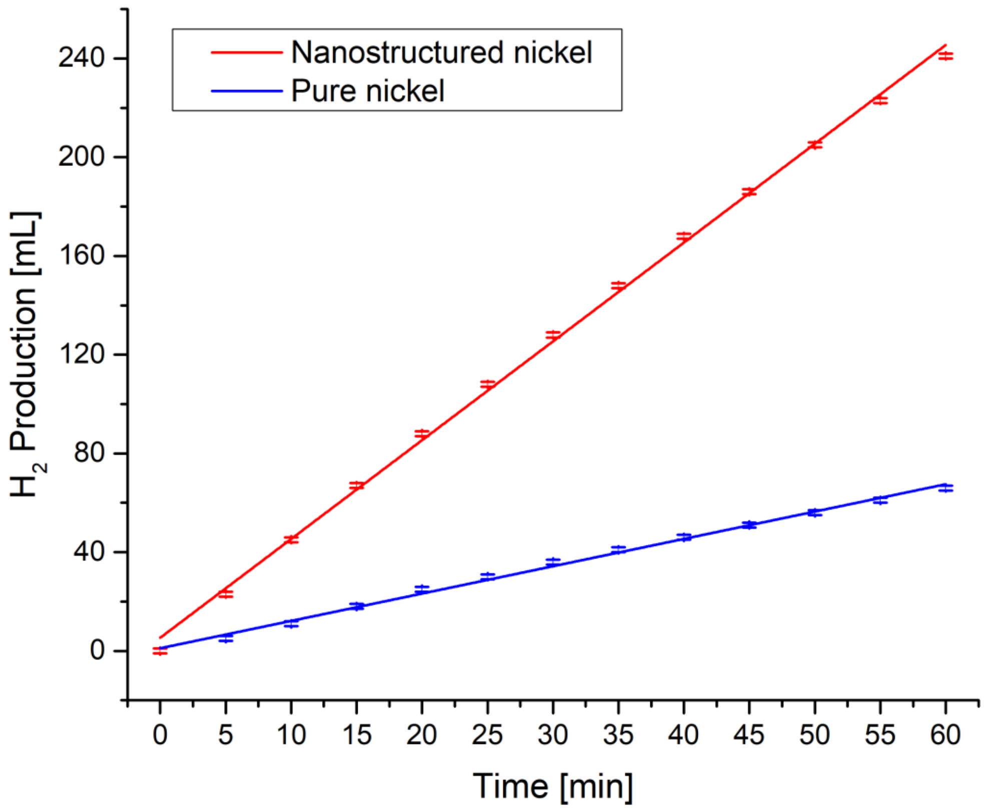

Figure 12: Cumulative Hydrogen production of the untreated Nickel compared to the Hydrogen production of a nanostructured electrode.

The Hydrogen production experiments showed remarkably promising results with the nanostructured electrode producing more Hydrogen gas by a factor of 3.7 compared to untreated Nickel electrodes. This result shows a remarkable enhancement of the Hydrogen production of nanostructured electrode in comparison to the non-nanostructured electrode. This enhancement has never been reported in the literature to our knowledge and thus it demonstrates the important application of laser nanostructuring using lasers in environmental friendly applications involving energy storage by Hydrogen production through alkaline electrolysis. Further investigations are ongoing in order to compare various samples with a varying degree of LIPSS contrast, various LIPSS classes (micro-conical, with spherical symmetry among others), 3D nanostructures extending into the bulk and also different material for the electrodes. Also, for the process of laser fabrication to be efficient and fast further improvement on the time management of the electrodes' production is needed. Broadening the laser beam that irradiates the Nickel samples may solve the time problem and therefore may be considered as a method for upscaling the fabrication process. Additional effects have to be taken into account since the low contrast and lower quality in the periodic nature of the formed LIPSS, as shown in Fig.9, possibly affects the chemical reaction that takes place during water electrolysis in ways that need further investigations.

7.3 Pulsed Laser Deposition Samples

The Nickel samples that were used for irradiation were commercial-grade Nickel sheets that have been subsequently treated with mechanical techniques in order to polish them and make their surfaces as flat as possible. However, there are certain limitations to the resulting surfaces. These exhibit a quite rough morphology as can be seen in Fig.13.

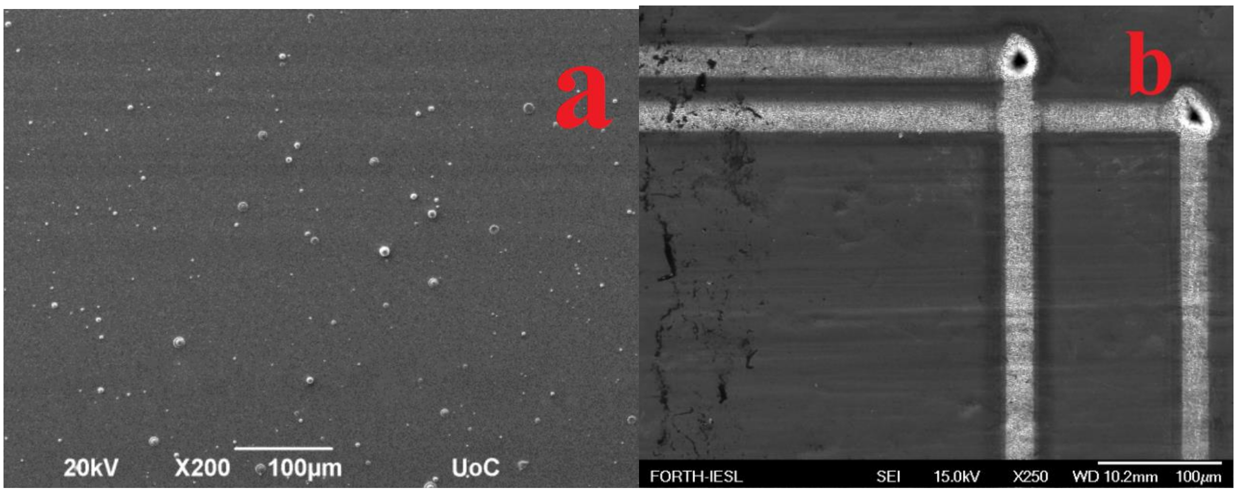

Figure 13: a) SEM image obtained from the surface of the PLD sample used for irradiation, **b)** SEM image obtained from the surface of a Nickel sample that was used for irradiation.

As shown in Fig.13a, the PLD grown Nickel sample shows an even and smooth surface with a few scattered spherical impurities that were formed during the creation of the sample. On the contrary, by observing the non structured surface of the Nickel sheet sample in Fig.13b, a variety of extended linear morphological inconsistencies can be seen. This unavoidably results to uneven irradiation during the laser creation of LIPSS. Also, the enhancement factor of 3.7 that has been found, is a result of the comparison of laser-nanostructured surfaces with a non-irradiated surface, which, as explained above, is not perfectly flat and attains a rather rough morphology. Thus, the factor 3.7 may very well be an underestimation of what can be achieved as far as Hydrogen production efficiency is concerned. Much higher quality surfaces can be prepared by employing the Pulsed Laser Deposition (PLD) technique.

Pulsed Laser Deposition (PLD) is a technique which uses a high power pulsed laser to irradiate and vaporize the target material in vacuum environment. The vaporized target material is then deposited on a substrate and forms a thin layer on the substrate used. Using Nickel samples produced with this technique will show the enhancement in Hydrogen production nanostructured Nickel electrodes provide when compared with a surface that shows minimal morphological defects. Additionally irradiating samples grown with PLD will show better results of the interaction the laser beam has with Nickel, since due to the lack of the morphological defects, the beam will irradiate the entire sample evenly.

Samples grown with PLD were used for irradiation, and the results are shown in Fig.14. As can be seen, LIPSS are also formed in these samples as well. Some peculiarities in the contrast of the observed LIPSS led us to suspect that the laser fabrication process did not only involve the deposited Nickel film but possibly the Silica substrate as well. These peculiarities arise from the observation that the darker areas in between the bright stripes (bright correspond to the peaks of the LIPSS) are flat and show no or little variation on the image brightness.

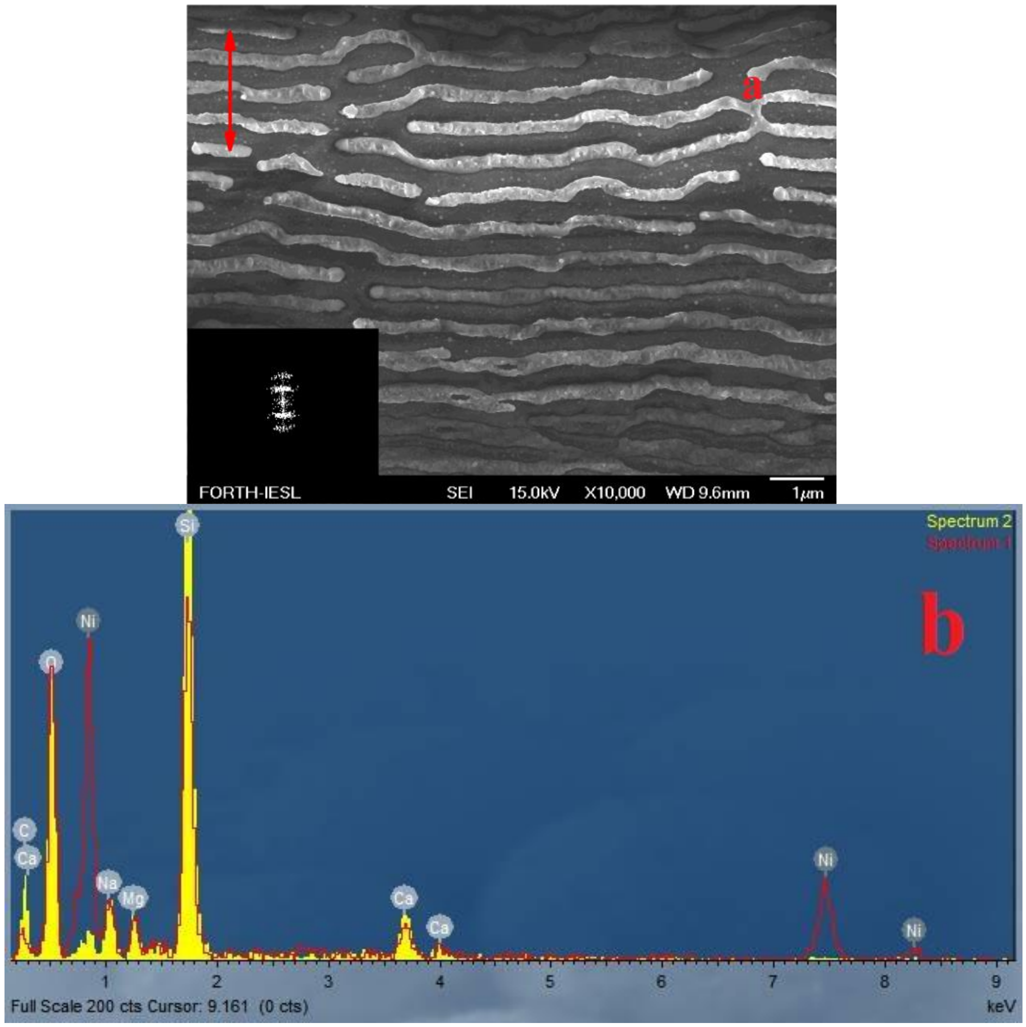

Figure 14: a) Nickel sample grown with PLD, **b)** results of the x-ray spectroscopy performed on a. The red graph shows the spectroscopic results produced by the bright areas shown in a, while the yellow graph shows the spectroscopic results produced by the dark areas shown in a.

To investigate this, we performed X-ray spectroscopy on the laser irradiated films. The analysis shows high concentration of silicon in both the bright (i.e. LIPSS peaks) (yellow graph) and the dark areas (i.e. LIPSS valleys) (red graph), while in the dark area (yellow graph) there is no Nickel present. Thus, we conclude that during irradiation the laser beam scrapped the entire film of Nickel that was deposited and reached to the glass substrate. The Nickel layer was about 300 nm thick, and thus thicker layers of Nickel must be created for future experiments to be conducted on PLD grown Nickel samples.

8. Conclusions

Laser treated Nickel samples for LIPSS production show great potential in the Hydrogen production industry. Enhancement of the effective area, as well as minimizing the bubble effect by helping the detachment of gas bubbles, lead to much higher Hydrogen production compared to pure Nickel electrodes by a factor of 3.7. The study on the morphological characteristics of the electrodes that favor water electrolysis showed that the contrast of the nanostructure periodicity may have a positive effect on Hydrogen production due to further enhancement of the effective surface area, as well as the creation of nanoparticles. This is promising, since the time consumed for the creation of nanostructured electrodes can be decreased without decreasing the effect nanostructured electrodes have in Hydrogen production. By shifting the lens and unfocusing the beam, a larger area of the electrode can be structured reducing the time consumed in electrode production. Nonetheless further studies on the morphological properties on electrodes need to be conducted to reach better results in the Hydrogen production industry. A parametric research was conducted proving that scanning direction does not affect the structures produced, while further and more thorough examination of the influence the incident number of pulses per spot have on the periodicity of the formed structures, is needed. There is a need of propositions to be made in order to implement faster ways of the electrodes' production. Broadening the beam by shifting the lens focusing the beam on the sample was implemented in the work which resulted in similar Hydrogen production with the electrodes that were fabricated using optimally focused laser beams. The structuring parameters of the nanostructured electrode that produced the results in Fig.12, $N=339\pm1$, $\varphi_0=1.4\pm0.1$ Jcm^{-2} and a line density of 25 μm. Additionally, further studies on materials other than Nickel should be conducted, as well as irradiation from different angles, creating different morphological patterns that might enhance the Hydrogen production further. The creation of PLD grown samples suitable for irradiation and LIPSS formation should also be studied further, so as to obtain a better understanding on the impact that LIPSS have. Further, 3D laser nanostructuring should be also considered for future studies. The results of this study show a great potential of laser nanostructured electrodes in the production of Hydrogen, which is of crucial importance for clean energy storage solutions.

Bibliography

1. MILLET, P. . &. G. S. Renewable Hydrogen Technologies. In: MILLET, P. . &. G. S. **Renewable Hydrogen Technologies**. [S.l.]: Elsevier, 2013. p. 19-40.

2. ZENG, K. . &. Z. D. Recent progress in alkaline water electrolysis for hydrogen production and applications. **Progress in Energy and Combustion Science**, v. 36, p. 307-326, 2009.

3. TSIBIDIS, G. D. . S. E. . L. P. A. . &. F. C. Controlled ultrashort-pulse laser-induced ripple formation on semiconductors. **Applied Physics A**, v. 114, p. 57-68, 2014.

4. BARBEROGLOU, M. . T. G. D. . G. D. . M. E. . F. C. . S. E. . &. L. P. A. The influence of ultra-fast temporal energy regulation on the morphology of Si surfaces through femtosecond double pulse laser irradiation. **Applied Physics A**, v. 113, p. 273-283, 2013.

5. LI, X. . &. G. Y. Theoritical fundamentals of short pulse laser-metal interaction: A Review. **Nanotechnology and Precision Engineering**, v. 3, p. 105-125, 2020.

6. FRAGGELAKIS, F. . S. E. . &. L. P. A. Control of periodic surface structure on silicon by combined temporal and polarization shaping of femtosecond laser pulses. **Applied Surface Science**, v. 444, p. 154-160, 2018.

7. YANG, Y. . Y. J. . X. L. . &. G. Y. Surface patterning on periodicity of femtosecond laser-induced ripples. **Applied Physics Letters**, v. 97, 2010.

8. BONSE, J. . H. S. . K. S. V. . R. A. . &. K. J. Laser-Induced Periodic Surface Structures— A Scientific Evergreen. **Journal of Selected Topics in Quantum Electronics**, v. 23, n. 3, 2017.

9. J. BONSE, J. K. S. H. A. R. Femtrosecond laser-induced periodic surface structures. **Journal of Laser Applications**, v. 24, n. 4, 16 July 2012.

10. NIELSEN, J. . B. . S. J. . M. . C. M. . S. . &. B. P. Ultra-short pulse laser ablation of metals: threshold fluence, incubation coefficient and ablation rates. **Applied Physics A**, v. 101, p. 97-101, 2010.

11. TSIBIDIS, G. D. . B. M. . L. P. A. . S. E. . &. F. C. Dynamics of ripple formation on silicon surfaces by ultrashort laser pulses in subablation conditions. **Physical Review B**, v. 86, n. 11, 2012.

12. LASEMI, N. . P. U. . Z. L. V. . B.-M. O. . L. R. . &. K. W. Pulsed laser ablation and incubation of nickel, iron and tungsten in liquids and air. **Applied Surface Science**, v. 433, p. 772-779, 2017.

13. BONSE, J. . W. J. M. . K. J. . &. K. W. Ultrashort-pulse laser ablation of indium phosphide in air. **Applied Physics A**, v. 72, p. 89-94, 2001.

14. HAMAD A., H. Effects of Different Laser Pulse Regimes (Nanosecond, Picosecond and

Femtosecond) on the Ablation of Materials for Production of Nanoparticles in Liquid Solution. In: HAMAD A., H. **Effects of Different Laser Pulse Regimes (Nanosecond, Picosecond and Femtosecond) on the Ablation of Materials for Production of Nanoparticles in Liquid Solution**. [S.l.]: [s.n.], 2016. Cap. 12.

15. WIKIPEDIA. **Surface Plasmon - Wikipedia**. Disponivel em: <https://en.wikipedia.org/wiki/Surface_plasmon>.

16. ALBU, C. . L. C. . &. Z. M. Periodical Structures induced by femtosecond laser on nickel in air. **Optoelectronics and Advanced Materials**, v. 8, p. 363-367, 2014.

17. MENG, F. . H. J. . H. W. . L. P. . &. W. Q. Morphology control of laser-induced periodic surface structure on the surface of nickel by femtosecond laser. **Chinese Optics Letters**, v. 13, n. 6, 2015.

18. GABLER, A. . M. C. . I. . R. T. . K. M. . K. B. . R. L. . &. S. W. Ultrashort pulse laser-structured nickel surface as hydrogen evolution electrodes for alkaline water electrolysis. **International Journal of Hydrogen Energy**, 2017.

19. GANCI, F. . L. S. . S. C. . &. I. R. Nanostructured electrodes for hydrogen production in alkaline electrolyzer. **Renewable Energy**, 2018.

20. RAUSCHER, T. . M. C. . I. . G. A. . G. T. . K. M. . K. B. . S. W. . &. R. L. Femtosecond-laser structuring of Ni electrodes for highly active hydrogen evolution. **Electrochimica Acta**, 2017.

21. ORDAL, M. . A. . L. L. . L. . B. R. . J. . B. S. . E. . B. R. . R. . A. R. . W. . &. W. C. . A. Optical properties of the metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti and W in the infrared and far infrared. **Applied Optics**, v. 22, n. 7, 1983.