High-speed laser surface texturing by combining direct laser interference patterning with polygon scanner technology

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Abstract

In this work, Direct Laser Interference Patterning (DLIP) is used in conjunction with the polygon scanner technique to fabricate textured polystyrene and nickel surfaces through ultra-fast beam deflection. For polystyrene, the impact of scanning speed and repetition rate on the structure formation is studied, obtaining periodic features with a spatial period of 21 µm and reaching structure heights up to 23 µm. By applying scanning speeds of up to 350 m/s, a structuring throughput of 1.1 m²/min has been reached. Additionally, the optical configuration was used to texture nickel electrode foils with line-like patterns with a spatial period of 25 µm and a maximum structure depth of 15 µm. Subsequently, the structured nickel electrodes were assessed in terms of their performance for the Hydrogen Evolution Reaction (HER). The findings revealed a significant improvement in HER efficiency, with a 22% increase compared to the untreated reference electrode.

1. Introduction

Surface modification of metallic and polymer materials by producing well-defined topographical elements is a highly interesting path to achieve advanced surface functionalities. This leads to the expansion of the potential range of applications in the fields of microfluidics, biomedical technology and electronics [1-3]. There is a wide variety of chemical and physical technologies available micropattern surfaces such as expensive photolithography, wear intensive micro contact printing and chemical etching [4]. Alternative approaches to typical manufacturing processes are laser texturing methods [5]. In particular, the Direct Laser Interference Patterning (DLIP) technology is considered to be a flexible and highly versatile solution for producing highly periodic and deterministic microstructures and thus for functionalizing surfaces. In this process, multiple coherent laser beams are superimposed and focused on a substrate's surface, resulting in the formation of an interference pattern with a periodic distribution of the laser intensity. Furthermore, by controlling the number of the applied laser beams and their overlapping angles, specific geometries and sizes can be produced by local ablation processes at the interference maxima positions [6]. In order to scale-up DLIP processes to industrial production, different beam manipulation systems have been developed aiming to increase process throughput. For example, by applying a static DLIP optical concept with an elongated beam profile, line-like patterns with a maximum throughput of 0.9 m²/min could be fabricated on polycarbonate by moving the substrate at 1 m/s [7]. Other technologies, such as polygon scanners, allow processing speeds of up to 1000 m/s, without the additional movement of the components. However, the disadvantage of this technology is the comparatively low resolution (~40 - 50 µm) due to the relatively large diameter of the laser beam at the focus position [8]. The aim of this work is to demonstrate the feasibility of combining polygon scanners with DLIP technique, increasing both resolution as well as throughputs reaching values over 1 m²/min. Furthermore, the optical configuration is employed to functionalize nickel electrodes, typically used for alkaline water electrolysis. In this context, the topography of the fabricated electrodes is characterized using optical confocal microscopy as well as scanning electron microscopy, combined with Fourier analysis. Also the electrochemical performance for the Hydrogen Evolution Reaction (HER) efficiency of the laser-treated electrodes is evaluated.

2. Experimental section

For the laser structuring experiments black polystyrene plates (PS) with lateral dimensions of 90 mm x 90 mm and 1.5 mm thickness and commercially nickel sheets (Goodfellow, USA) with a size of 300 mm × 300 mm and a thickness of 0.125 mm were utilized. Before laser structuring the samples were cleaned from contamination with 99.5 % ethanol solution (Supelco, Germany).

The laser structuring through DLIP was realized as described in [12]. The setup consists of a picosecond solid-state laser (Innoslab PX/FX, EdgeWave, Germany) with a maximum pulse energy of 270 µJ and maximal average laser power of 470 W. The laser wavelength was 1064 nm and the pulse duration 12 ps. The beam emitted from the laser source is later expanded using a telescope system and then split into two sub-beams by a Diffractive Optical Element (DOE). In order to achieve high scanning speeds, a polygon scanner (PM series, Moewe, Germany) was utilized. The deflected sub-beams are focused onto the material surface by a 420 mm f-theta objective lens. With this optical configuration, the spatial period Λ of the interference pattern was set to 21.0 µm and 25.0 µm [9,10]. Finally, confocal microscopy images (Sensofar S-Neox, Spain) were captured to evaluate the surface topography of the laser-structured samples. For a more detailed analysis of the surface topography, Scanning Electron Microscopy (SEM) was performed using Zeiss Supra 40VP (Carl Zeiss, Germany). The electrochemical characterization of the treated Ni-electrodes was performed in a conventional three-electrode cell configuration under industrial conditions with 30wt.-%. KOH [13]. The activity towards HER was analyzed by overpotential (η_{HER})-time curves and steady-state polarization curves. Further information has been published elsewhere [10].

3. Results and discussion

3.1. DLIP-polygon based surface structuring

For the first set of experiments, DLIP line-like textures were produced on black PS with a spatial period of 21.0 µm. As process parameters, the scanning speed v_{scan} and the laser repetition rate f_{rep} were varied to investigate the changes of the structure morphology depending on the mentioned parameters.

The SEM images in Figure 1a and c show multiple line scans with the corresponding DLIP features. The single scan lines are spaced by 75 µm. Confocal images shown in Fig. 1b and d correspond to the same samples displayed in Fig. 1a and c, respectively. Using a scanning speed of 200 m/s (Figs. 1a and b) and a repetition rate of 5 MHz (resulting in a cumulated fluence Φ_{cum} = 2.8 J/cm²), well-defined periodic lines with a structure height of 6 µm were fabricated. The structure formation was caused by local swelling of the polymer material at the positions corresponding to the maxima of the interference pattern. The origin of the swelling of the material is the absorption of the IR radiation by the black dye within the polymer matrix, that leads to the formation of gaseous by-products, internal pores in the polymer and ultimately to the expansion of the material towards the surface. This phenomenon has already been observed in other publications [7]. At higher cumulative laser fluences of Φ_{cum} of 8.3 J/cm² (obtained with scanning speeds v_{scan} of 100 m/s), the irradiated areas display a more profound modification of the material surface, with the formation of features with heights between 5 and 12 µm. In this case, the structure formation is driven by a combination of swelling and ablation mechanisms (Fig. 1c, d).

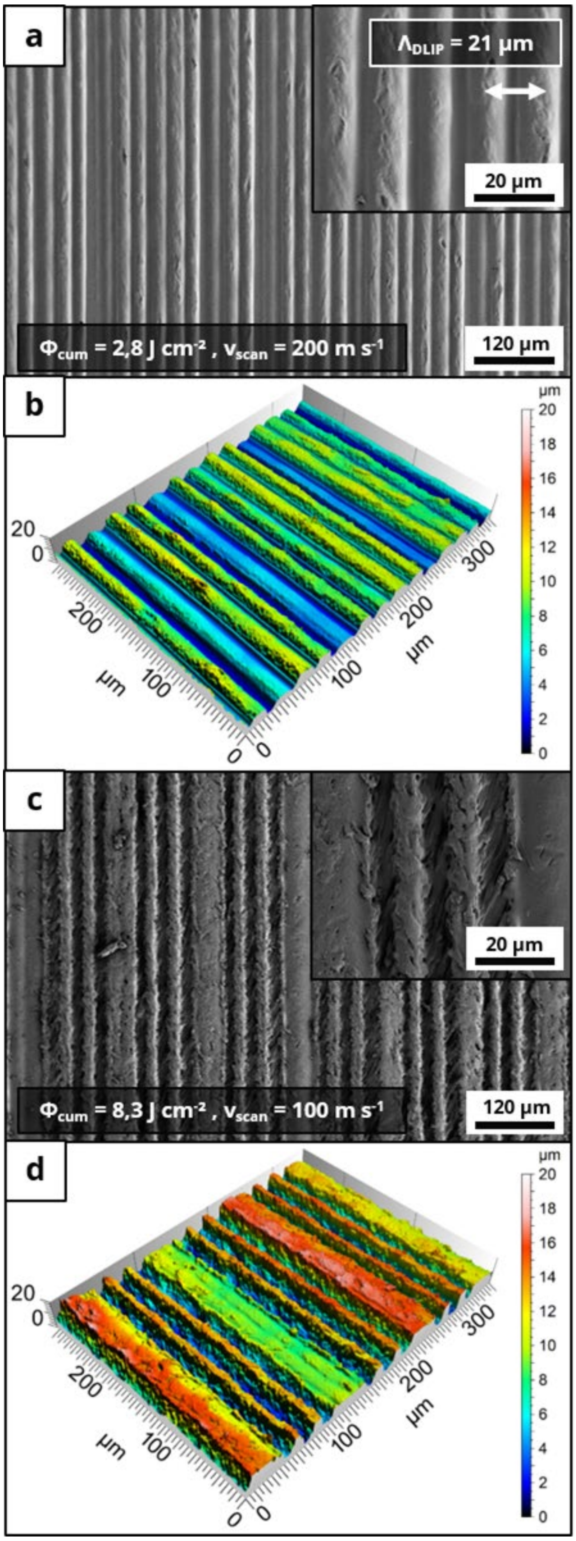

Figure 1: SEM images (a, c) and corresponding 3D CM (b, d) of DLIP structured polystyrene at a repetition rate f_{rep} of 5 MHz and different scanning speeds: Φ_{cum}= 2.8 J/cm², v_{scan}= 200 m/s (a, b); Φ_{cum}= 8.3 J/cm², v_{scan}= 100 m/s (c, d); spatial period Λ = 21.0 µm.

The dependency of the resulting structure height with the applied scanning speed at different repetition rates (2 to 5 MHz) is shown in Fig 2.

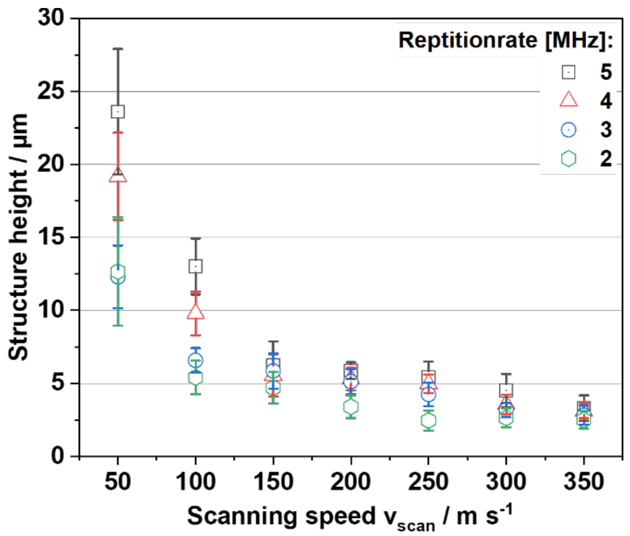

Figure 2: Structure height in dependence of scanning speed and repetition rates frep. Modified from [9].

The largest structure heights were achieved for a scanning speed of 50 m/s, ranging from ~ 12 to 23 µm depending on the applied repetition rate f_{rep}. Whereby the resulting structure height values for the respective repetition rates show a large deviation, indicating a higher irregularity of the surface topography. The decrease in height as the scanning speed increases can be explained by examining the cumulative laser fluence for each parameter set. In case of slower scanning speeds, a higher number of laser pulses per time unit accumulate within a certain area, causing a larger amount of polymer to swell at the maximum positions. On the other hand, higher repetition rates resulted into higher structures, which indicates that pulses with lower fluences per pulse are more suitable to swell the structures efficiently.

For the sample structured at scanning speeds above 200 m/s, the structure height varied from about 3 to 6 µm, depending on the repetition rate. Furthermore, slight deviations in the height of the structures were observed (see error bars), indicating a more homogeneous surface topography.

In addition to the evaluation of the structure heights, the maximum process throughput was determined. The process throughput has been calculated taking into consideration the scanning speed, the separation distance between the scanned lines and the duty cycle of the polygon (~50 %). For scanning speeds of 50 and 350 m/s in combination with a line spacing of 75 µm, throughput rates of 0.11 and 0.79 m^2/min could be achieved. For an additional increase in the process throughput, the separation distance was raised to 100 µm, resulting in 1.1 m^2/min.

3.2. Nickel electrode functionalization

Line-like DLIP features were produced on Ni-electrodes with spatial period 25.0 µm. As process parameters, the scanning speed v_{scan} as well as the number of consecutive passes N were varied. In this way, the cumulated laser fluence could be controlled (for further details refer to [10]).

Exemplary results of produced topographies are shown in Figure 3. For instance, the line-like patterns with 25.0 µm period produced using a cumulated fluence (Φ_{cum}) of 32 J/cm² show not only a well-defined array of grooves ablated at the maxima positions of the interference pattern but also the formation of regular wavy nanostructures known as Laser-induced Periodic Surface Structures (LIPSS). These features are located on the maxima positions of the interference pattern (see insets in Figure 3) and are oriented perpendicularly to the laser polarization (arrows in the insets). In addition, also for the spatial period Λ of 25.0 µm, periodic micro-holes with a diameter of 1.4 ± 0.3 µm are visible, when using higher cumulated fluences (Φ_{cum} = 640 J/cm²), see Figure 3b. Furthermore, the appearance of the micro holes affected the straightness of the line-like pattern and led to irregular DLIP micro channels.

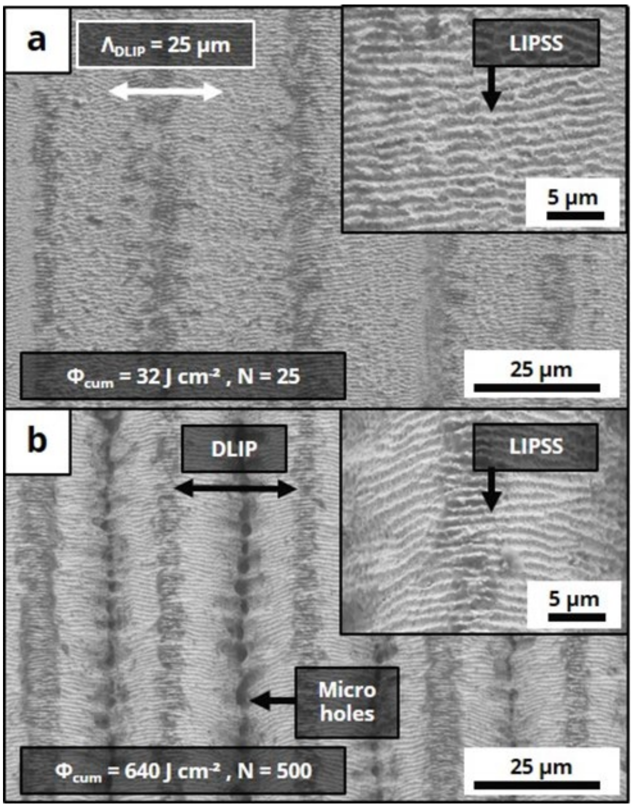

Figure 3: Exemplary SEM images of DLIP line-like structures produced on nickel at a repetition rate of 8.4 MHz and scanning speed of 200 m/s (modified from [10]).

Using optical confocal microscopy analysis, the dependence of the structure depth as a function of the consecutive passes was determined, as shown in Figure 4. The structure depth of the line-like surface patterns (Figure 4) increased consistently with the number of consecutive passes, as expected. The deepest structures for the line-like textures were achieved at a scanning speed of 200 m/s. The relationship between structure depth and scanning speed can be explained in terms of the cumulated laser fluence (Φ_{cum}). Lower structuring speeds result in a higher overlap of laser pulses and thus higher cumulated fluence per position. As a consequence, more material is ablated at the interference maxima positions leading to deeper structures. In general, variations of the structure depth ranging from 1 µm to 13 µm were observed for the line-like patterns

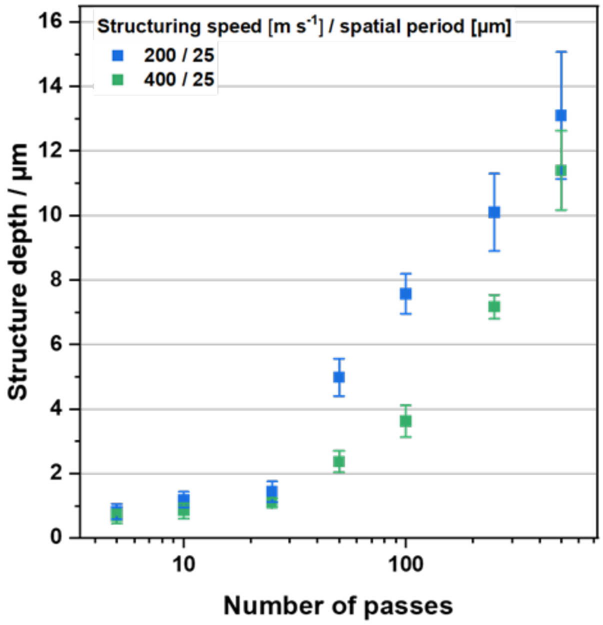

Figure 4: Structure height in dependence of scanning speed and number of consecutive passes. Modified from [10].

3.2. Preliminarily electrochemical characterization

Finally, the evaluation of the electro-catalytic activity towards HER in an alkaline medium was conducted on the line-like DLIP-structured nickel electrodes. The results of the investigation for the overvoltage potential are displayed in Figure 5.

The evaluated DLIP samples have a structure period of 25.0 µm and differ in the number of successive passes N. The aim was to determine the influence of the number of passes on the corresponding overvoltage potential (η_{HER}).

All recorded curves showed an increasing overpotential over time, whose slopes tend to slow down after 20 to 25 minutes. The increase in the overpotential during the first stage of HER might be related to the reduction of native oxides or hydroxides as well as the formation of a thin nickel hybrid layer of few atoms [11]. In Figure 5, it can be concluded that treating the nickel electrode with DLIP led to significant shift of the overpotential-time curves towards lower overpotential values. Furthermore, it can be noted that the decrease in overpotential is proportional to the number of consecutive passes employed during the fabrication process. This overpotential yield (up to 361 ± 21 mV) denotes an increase of the efficiency of the electrodes for producing hydrogen of 22%.

Further details about the electrochemical results and discussion can be found in [10].

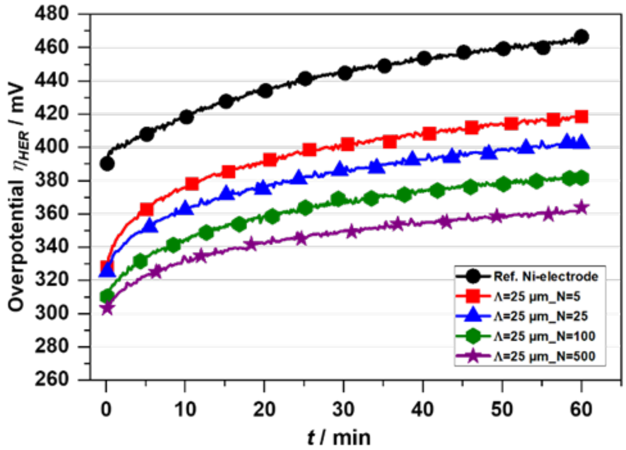

Figure 5: Overpotential-time curve of the hydrogen evolution reaction on the line-like patterned foils compared to the untreated reference at a geometric current density of -0.5 A cm ^{2} in 30wt.% KOH at 333 K for a period of 1 h (modified from [10]).

4. Conclusion

In this work, the combination of Direct Laser Interference Patterning and polygon scanner technologies was demonstrated on nickel and polystyrene substrates. Using a high-power picosecond laser source, in conjunction with two-beam DLIP setup, periodic micro structures with line-like geometries could be produced. In this context black polystyrene plates were treated at scanning speeds between 50 and 350 m/s, showing the viability of the process. Line-like patterns exhibiting a spatial period of 21.0 µm and structure heights up to 23 µm were induced either by the local swelling of the material at low cumulated fluences, or by a combination of ablation and swelling at higher fluences. The method allowed reaching outstanding throughputs up to 1.1 m^2/min. Furthermore, nickel foils were textured with line-like patterns with a spatial period 25.0 µm and a maximum structure depth of 13.1 µm. The line-like DLIP-treated samples were employed as electrodes in hydrogen evolution reaction experiments. The results demonstrated that the samples with the most significant increase in surface area exhibited a substantial reduction in overpotential, reaching up to 22% compared to the reference flat Ni electrode.

Acknowledgments

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