

On the tailoring of biomaterials by femtosecond pulse laser and plasma-based polymerization of functional coatings

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Abstract: Laser- and plasma-induced changes in the surface morphology and chemistry respectively, were carried out to improve the biocompatibility of surfaces aimed at biomedical applications. In this work, surface structuring by means of a femtosecond pulse laser and plasma polymer deposition were conducted. The obtained surfaces were analysed in terms of topography and chemical composition whereas the biocompatibility was tested by analysing the cell behaviour toward the modified and/or coated surface.

Keywords: atmospheric pressure plasma polymerization, laser structuring, biocompatibility, biomaterials

1. Introduction

Biocompatibility is the most crucial criteria for successful implant integration in orthopaedic surgery and dentistry. Titanium and its alloys possess good biocompatibility, excellent mechanical properties (non-corrosive, wear-resistant) and good chemical stability making them the most employed biomaterials for implants. Yet, even these materials must undergo various treatments to improve their current surface properties. Surface characteristics strongly modulate the cell behaviour. Wettability strengthens bio-response; therefore, hydrophilic surfaces must be achieved [1].

Various laser-based and plasma-based techniques for surface modification have been developed to enhance biocompatibility and osseointegration [1-7]. Kumar et al. investigated the effect of laser texturing on the wettability of Ti6Al4V implants by the means of a nanosecond pulse fibre laser. At specific parameters, a wetting behaviour was observed with the increase of structures from lines (hydrophobic surface) to complex grids (hydrophilic surfaces) [5]. Moerke et al. demonstrated that cells tended to preserve their osteoblast-specific function on micropillar surface [6]. Cell spreading in the patterns expressed a higher cell-surface contact after plasma polymerized allylamine layer was deposited on the titanium pre-coated silicon samples.

Despite the myriad of research proposals and results, the optimal geometric morphology satisfying a fast and efficient osseointegration has not been defined. In the present study, a two-step process approach for surface modification of implant material is introduced. The objective of this work is to investigate the cellular response depending on surface morphology and chemistry, respectively.

Two experimental methods were employed: Firstly, the surface was structured by a laser to adjust a certain micro roughness and secondly, a biocompatible plasma polymer coating was deposited on the structured surface by using an atmospheric pressure plasma jet.

where analysed in terms of morphology, wettability, surface chemistry and biocompatibility.

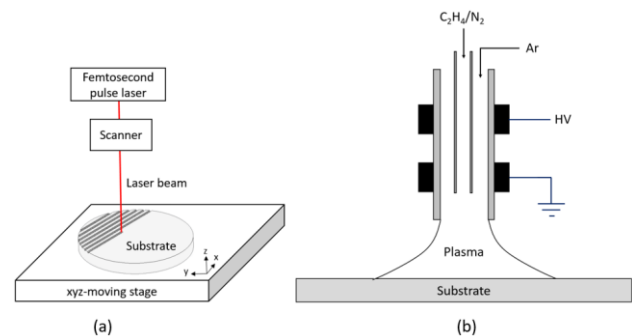


Fig. 1. Scheme of the experimental setup for (a) laser structuring and (b) plasma polymer deposition.

2. Methods

Ti6Al4V disks were used in these experiments. Prior to treatment, the substrates were ultrasonically cleaned in isopropanol for 1 minute and dried with air. Each sample was placed onto a substrate holder mounted on a three-axis (x, y, z) moving table.

Microstructures were performed by the means of a femtosecond pulse laser at a wavelength of 1030 nm. The system was coupled with a scanner focusing the laser beam on the substrate surface (Fig. 1.a). The focal length of the lens is 100 mm. Based on the work Moerke et al. [6], micropillars with different spatial periodicities were generated by varying the process parameters such as laser power, pulse energy, pulse repetition frequency and scan speed. The pulse duration remained constant at around 300 fs. The sample were positioned perpendicularly under the scanner at the focal point.

The plasma polymer deposition was performed at room temperature using an atmospheric pressure plasma jet coupled to a power supply operating at a RF of 13.56 MHz. The plasma source was composed of two capillary tubes, an inner one made of aluminium oxide and an outer glass tube surrounded by two ring electrodes (Fig. 1.b). The

plasma was generated by using argon. The precursor comprises a mixture of ethylene and nitrogen and was introduced into the argon plasma via the inner capillary. The substrate was placed under the nozzle at a distance of 2 mm.

The surface topography was examined by using a Scanning Electron Microscope (SEM). The chemical composition of the plasma polymerized layer was analysed by X-ray Photoelectron Spectroscopy (XPS). The wettability nature of the samples was determined by water contact angle (WCA) measurements.

3. Results

Micropillars with average dimensions of 4 μm in height and 40-50 μm in width are obtained (Fig. 2).

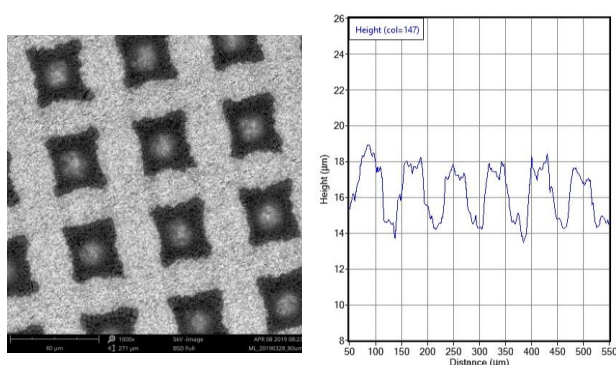


Fig. 2. Top view of the structured surface (left) along the surface profile (right)

The deposited thin polymerized layer comprises nitrogen-based and oxygen-based functional groups (Fig. 3), which are known to promote cell adhesion and proliferation [8, 9]. Additionally, water contact angle measurements reveal an improved wettability on both, the structured and the coated surfaces, respectively.

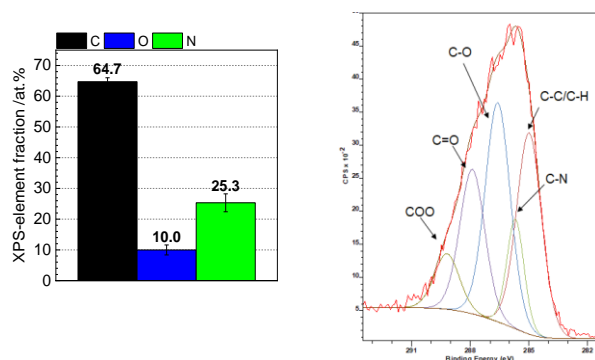


Fig. 3. XPS analysis of the elemental composition (left) and peak fit of the C 1s core level spectrum (right) of the plasma polymerized layer

4. Conclusion

Consequently, by using a femtosecond laser, micrometer sized spike structures as functional surfaces for cell controlling was generated. The spike dimensions as well as

the average spike-to-spike distance can be easily tuned by varying the process parameters. Furthermore, the surface reveals hydrophilic properties required for cell adhesion. The plasma-generated thin polymer film provides the functional groups, especially nitrogen-based moieties, to further improve the biocompatibility of the modified surface. Imminent cell studies will give some indications of the cell adhesive properties of the modified surfaces.

5. Acknowledgement

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6. References

- [1] H.-Y. Lee et al., *Appl. Sci. Conver. Technol.*, 25 (3), 55-55 (2016)
- [2] F. Rupp et al., *Dental materials*, 34, 40-57 (2018)
- [3] N. B. Dahotre et al., *Phil. Trans. R. Soc. A*, 368, 1863-1889 (2010)
- [4] N. R. Danna et al., *BioMed Research International*, Vol. 2015, 761718 (2015)
- [5] N. Kumar et al., *IOP Conf. Series: Materials Science and Engineering*, 149, 012056 (2016).
- [6] C. Moerke et al., *Journal of Cell Science*, 131 (2018)
- [7] K. Fricke et al., *On the Deposition of Bactericidal Copper/Plasma Polymer Composite Coatings by using Atmospheric Pressure Plasmas (abstract)*, 23rd International Symposium on Plasma Chemistry, July 31st – August 4th (2017).
- [8] H. Testrich et al., *Materials Science and Engineering C* 33, 3875-3880 (2013)
- [9] Y. Arima, H. Iwata, *J. Mater. Chem.*, 17, 4079-4087 (2007)