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Matrix-Assisted Pulsed Laser Evaporation of Organic Thin Films: Applications in Biology and Chemical Sensors

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<http://dx.doi.org/10.5772/intechopen.70676>

Abstract

Polymer and biomolecule processing for medical and electronics applications, i.e. the fabrication of sensors and biosensors, microarrays, or lab on chip devices is a cornerstone field which shows great promise. Laser based thin film deposition techniques such as pulsed laser deposition or matrix-assisted pulsed laser evaporation (MAPLE) are competing with conventional methods for integrating new materials with tailored properties for novel technological developments. Successful polymer and protein thin film deposition requires several key elements for depositing viable and functional thin films, i.e. the characteristics of the laser depositing system, the choice of targets and receiver substrates, etc. This chapter reviews the following topics: brief presentation of the MAPLE process including several examples of polymer materials deposited by MAPLE, thus illustrating the potential of the technique as a gentle laser-assisted deposition method. In particular, the “synthesis” of new materials, their analysis and correlation of the bulk and interface properties to its bio-environment shall be discussed as a method to tackle some bioengineering issues. We will also focus on recent breakthroughs of the MAPLE technique for the fabrication of functional devices, i.e. sensor devices based either on chemoresponsive polymers or on proteins.

Keywords: maple, polyethylenimine, polyepichlorohydrin, polyisobutylene, lactoferrin, odorant-binding proteins, saw, hydroxyapatite nanoparticles, ha, polyethylene glycol-co-polycaprolactone methyl ether, PEG-PCL-me

1. Introduction

A little more than 50 years ago, on 16 May 1960, *LASER* light was first generated, at the time being described as “*a solution looking for a problem.*” Today, this acronym for *Light Amplification*

by *Stimulated Emission Radiation* has become a common part of our vocabulary. The properties of emitted light make lasers useful devices in many applications where monochromatic, coherent light is required. The use of lasers today is so far reaching and widespread that a comprehensive enumeration is impossible. Lasers cross many areas of manufacturing, such as medicine, surgery, telecommunications, homeland security, lighting, displays, and nano-technology, just to name a few.

New tools bring new capabilities to research. In materials science, laser techniques revolutionized our understanding of materials by making it possible to design and integrate new materials with tailored properties for novel technology developments. Shortly after the discovery of lasers, researchers began irradiating every possible target material and phase.

Three years after the discovery of laser, Breech and Cross studied the laser vaporization and excitation of atoms from solid surfaces, while in 1965, Smith and Turner deposited the first thin films using a ruby laser. Starting with that moment, laser ablation became more and more popular for the deposition of various materials as thin films.

Pulsed laser deposition (PLD) is a growth technique that has been extensively used over the years, in different configurations. The common principle of these different approaches relies on irradiating a target (solid or liquid) with a pulsed laser source that is powerful enough to produce the ablation of the respective target. As most PLD experiments are carried out in vacuum, in a specialized deposition chamber, the ablated species are ejected from the target in the form of plasma, commonly referred to as “ablation plume.” The high kinetic energy of the plume species (up to 100 eV) ensures their fast transport to a collecting substrate, usually positioned few centimeters away from the target. Ultimately, the ablated material gradually accumulates on the substrate in order to form a thin film, whose properties can be tuned by an appropriate control of the various experimental conditions.

Although the PLD technique is simple in concept, the flexibility in tuning the different parameters that affect the properties of the resulting films gives it a high degree of sophistication, which results in many advantages: (i) the laser source is positioned exterior to the deposition chamber, making it easy to operate changes to the ablation geometry and to deposition parameters involving ablation wavelength, energy per pulse, or the use of multiple ablation sources; (ii) most known solids and liquids have ablation thresholds well within the capabilities of present-day lasers dedicated to ablation procedures; (iii) for a given set of experimental parameters, the ablation rate of a target can be determined, which allows for a precise control of the film thickness down to a single pulse; (iv) a selective ablation of the target is achieved, limited to the area irradiated by the laser; (v) stoichiometric transfer between target material and substrate is achievable under appropriate conditions; (vi) the high kinetic energy of the ablated species provides them increased mobility, with respect to non-ablation techniques, thereby decreasing the substrate temperature that is otherwise necessary for the formation of a specific compound; (vii) PLD allows the obtaining of peculiar materials and metastable states that cannot be reproduced by other techniques [1, 2].

The ablation threshold of most target materials is well below that of their decomposition. However, there are several types of polymers, biopolymers, and proteins for which this condition does not hold true. These materials are very sensitive to pulse energies commonly delivered by ablation laser systems, and their direct irradiation, even at low fluence, can result in photochemical or thermal decomposition. Therefore, in order to avoid permanent structural damage, a softer laser ablation technique has been tailored around the specificities of organic and polymeric materials. This novel technique is referred to as “matrix-assisted pulsed laser evaporation” (MAPLE) and has been shown to be a powerful tool for the obtaining of organic thin films [1, 3]. In principle, it is a variation of the PLD concept, but its peculiar target preparation and handling procedures set it apart from a technical point of view. In MAPLE, the material of interest (e.g., a polymer or biomolecule) is diluted or dispersed in an inert solvent (i.e., matrix), and its weight concentration in the resulting solution is typically in the range of 0.1–5%. The solution is homogenized by means of magnetic stirring, and then frozen on a liquid nitrogen-cooled support, thus resulting in a solid target. When the target is ablated by the laser pulses, the solvent evaporates and is pumped out, whereas the material of interest (polymer, biomaterial) acquires sufficient kinetic energy to be transported and collected on the substrate. This approach provides a mechanism for thin-film growth that avoids structural damage of the dissolved material, due to the fact that the energy of the laser pulse is absorbed selectively by the solvent.

Two critical conditions must be fulfilled in order to achieve successful deposition by MAPLE:

1. The matrix should exhibit a strong absorption profile at the laser wavelength, whereas the guest material should show as little absorption as possible.
2. There must be no photochemical-mediated interaction between the solvent and the material of interest.

The most important advantages of MAPLE are (i) ultra-high vacuum is not required (a base pressure of 10^{-5} – 10^{-6} mbar is enough) and (ii) this method is very flexible for the selection of the solvents. If we have a material that can be dissolved in a solvent, we can try to apply MAPLE to produce thin films, but we have to consider the two conditions mentioned above.

Previous studies have shown that by a careful choice of the experimental conditions, that is, choice of laser wavelength, pulse length, laser fluence, substrate temperature, and background atmosphere, it is possible to deposit a wide range of organic and biological compounds, without any chemical or structural alterations. Here, we only present a reduced list of such materials: polymers (polyethylene glycol (PEG) [4, 5], poly(D,L-lactide) [6], polyalkylthiophene [7], polyaniline [8]), polymer blends [9], active proteins (lysozyme [10], lactoferrin [11], mussel protein [12]), nanoparticles (TiO_2 and SnO_2 [13, 14]), and polymer-carbon nanotube composites [15, 16].

Moreover, MAPLE has been successfully used in sensor applications. Several groups have successfully deposited different polymers for sensor applications. For example, in [17], Pique

et al. prove the suitability of MAPLE for the deposition of chemoselective polymers such as a fluoroalcoholpolysiloxane polymer (SXFA), and [18] demonstrated the deposition of polysiloxane thin films with applications in chemical sensors.

Although in the above-mentioned cases MAPLE has demonstrated its suitability for obtaining organic thin films, the deposition mechanism is still not completely elucidated. In [19, 20], molecular dynamics (MD) studies are performed for molecular systems consisting of polymer molecules dissolved in a volatile molecular matrix. The MD studies revealed a significant influence of the polymer molecules on the ablation process, even at relatively low concentrations in the range of several weight percent. Characteristic features detected on the surface of the MAPLE-deposited thin films such as elongated viscous droplets and “molecular balloons” composed of polymer layers which enclose matrix material were explained by these MD studies.

This chapter reviews the MAPLE process for the deposition of different types of materials (in particular polymers and proteins) as thin films for applications in biology and also their integration in sensor devices. Specifically, the following topics will be discussed: the experimental part in the MAPLE process for the deposition of polymer thin films; several examples of polymer materials deposited by MAPLE, illustrating the potential of this technique as a gentle laser-assisted deposition method. We will also focus on recent breakthroughs of the MAPLE technique for the fabrication of functional devices, that is, sensor devices based either on chemoresponsive polymers or on proteins, and biomedical applications of polymer thin films, that is, multifunctional active and responsive biointerfaces, coatings for orthopedic applications, biodegradable and non-biodegradable coatings as antitumoral systems.

2. MAPLE of polymers and proteins for sensor and biosensor applications

In the following section, we will address couple of recent breakthroughs of the MAPLE technique for the fabrication of functional devices, that is, sensor devices based either on chemoresponsive polymers or on proteins.

The detection of the analyte is based on the interaction between the polymer and target molecules which depends on the formation of a weak hydrogen bonding. The functional polymer group comprises a hydrophilic group, that is, a hydroxyl (OH) unit (or may be an NH_2 unit) and a hydrophobic group (e.g., fluorinated (CF_n) or siloxanes groups $-\text{Si}-\text{C}-\text{O}-\text{Si}-$ or $-\text{Si}-\text{O}-\text{Si}-\text{C}-$) which repel water due to the unpolar nature. The (OH) unit binds a single oxygen atom within the target analyte molecule, and a weak hydrogen bond is thus formed.

The first example of functional sensors presented in this work is based on the works published in [21–23]. Three polymers have been chosen, that is, polyepichlorohydrin (PECH), polyisobutylene (PIB), and polyethylenimine (PEI) to be used as chemical interactive membranes for the fabrication of surface acoustic wave (SAW) sensors. These polymers have the

ability to specifically and selectively identify target gases immediately, and in addition, they can be dissolved in common solvents, that is, PECH in acetone, PIB in toluene, and PEI in ethanol, which makes the fabrication of MAPLE targets rather easy.

In order to carry out the MAPLE experiments, the polymers (three independent experiments) were dissolved in the appropriate solvents at concentrations between 0.1 and 2 wt%, and the as-obtained solutions were flash frozen in liquid nitrogen. The polymer-containing targets were irradiated with a laser beam from a "Surelite II" pulsed Nd:YAG laser (Continuum Company, 266 nm wavelength). When laser light irradiated this target, the solvent evaporated and the polymer material was collected on the Si(100) substrate placed parallel and at 4 cm distance from the frozen target. All substrates were cleaned prior to any deposition by dipping them in different solvents, that is, first in acetone, followed by ethanol and finally in the ultrasonic bath with ultrapure water. The last step was to blow dry them in a nitrogen flow.

The laser fluence was varied between 0.08 and 0.8 J cm⁻². The substrates were kept at ambient temperature during the deposition. The number of pulses was varied from 6000 pulses to 54,000, resulting in thin polymer films (of PEI, PIB, and PECH) with variable thicknesses (between 40 and 300 nm). A frozen target during irradiation in a MAPLE experiment is shown in **Figure 1**.

Prior to their use in SAW sensor applications, the polymer films produced by MAPLE have been investigated from the surface morphology and chemical structure point of view. Atomic force microscopy (AFM) has been used to analyze the roughness and thickness of the deposited polymer films. AFM (XE 100 AFM setup from Park) measurements were carried out to analyze the films surface roughness on several different areas and dimensions. The chemical structure has been tested with Fourier transform infrared spectroscopy (FTIR). FTIR is a chemical analysis method that detects the characteristic vibrations of functional groups in a sample. The infrared spectrum of the native molecule was measured and compared with the thin-film spectra. The FTIR measurements were carried out with a Jasco

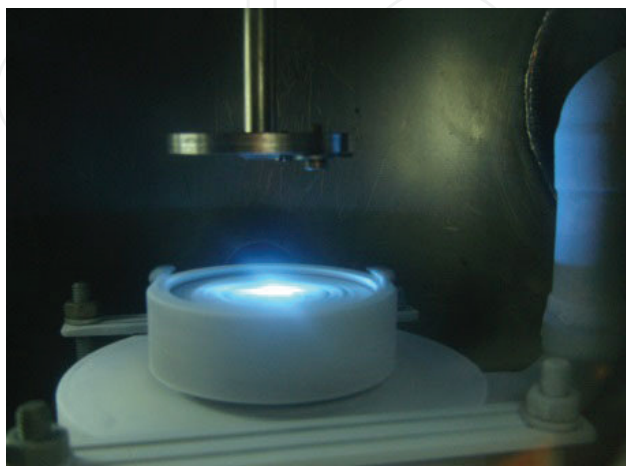


Figure 1. Picture taken during a typical MAPLE deposition.

FT/IR-6300 type A spectrometer in the range 500–7000 cm^{-1} . All spectra were obtained by accumulating 128 scans and $\text{CO}_2/\text{H}_2\text{O}$ correction.

Investigating the morphology of the deposited polymer (PIB, PECH, and PEI) films, it has been noticed that their quality is in general affected by the laser fluence, while the thickness of the deposited layers is related to the number of pulses. As general comments, it has been seen that there is an optimum range of laser fluences for which the surface of the thin polymer films deposited by MAPLE is uniform, with a low density of droplets and cracks. For example, the PIB thin films deposited by MAPLE on silicon substrates were generally rough, the best depositions were achieved for fluences between 0.1 and 0.3 J/cm^2 , with 0.08 J/cm^2 being the threshold laser fluence. For SAW sensor applications, polymer layers with low roughness are required, due to the fact that SAW scattering and diffraction can be minimized with a less rough active surface. This was achieved by using targets with polymer concentrations of 1 wt% and laser fluences of 0.1 J/cm^2 (in the case of all three polymers) for evaporation. 2D topographical AFM images of the three polymers deposited by MAPLE from targets containing 1 wt% polymer in the solution are shown in **Figure 2**. The laser fluence applied for the deposition was 0.1 J/cm^2 .

Further on, FTIR analysis was applied to investigate the chemical structure of polymer films. It has been found that for the laser fluences applied, where the polymer films are uniform and exhibit the lowest roughness (i.e., 0.1 J/cm^2), the important infrared active bands are very well reproduced (see **Figure 3** and **Figure 4** as examples).

In conclusion, MAPLE was successfully used to grow uniform and continuous polymer (PEI, PIB, and PECH) thin films which maintain their chemical structure similar to that in bulk. In order to prove their feasibility in SAW sensors, the polymer films were deposited onto SAW sensors and tested to evaluate the performances with respect to sensitivity, resolution, and response time. The responses of the PEI-, PIB-, and PECH-coated devices to different concentrations of dimethyl methylphosphonate (DMMP) were evaluated. The frequency shift of the bare and PIB-coated SAW sensor prior to being tested for DMMP analyte is shown in **Figure 5** (left). The response curve of the SAW sensor coated with PECH, PIB, and PEI polymer exposed to different concentrations of DMMP vapor in N_2 is shown in **Figure 5**.

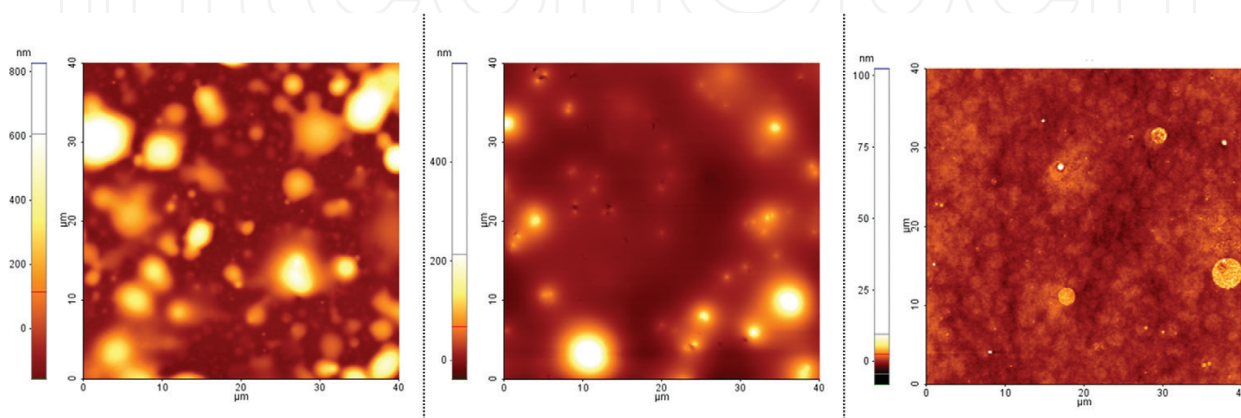


Figure 2. AFM images on a 40 × 40 μm areas of (left) PIB, (middle) PECH, and (right) PEI polymers.

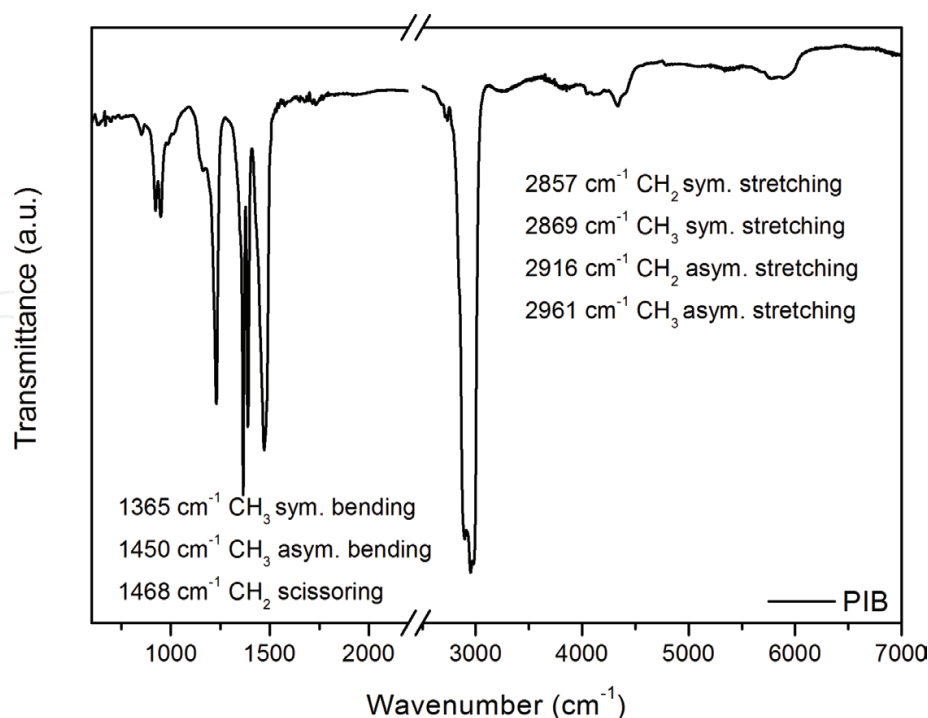


Figure 3. FTIR spectra of the PIB polymer layer deposited at a laser fluence of 0.1 J/cm² (for band assignment, see [24]).

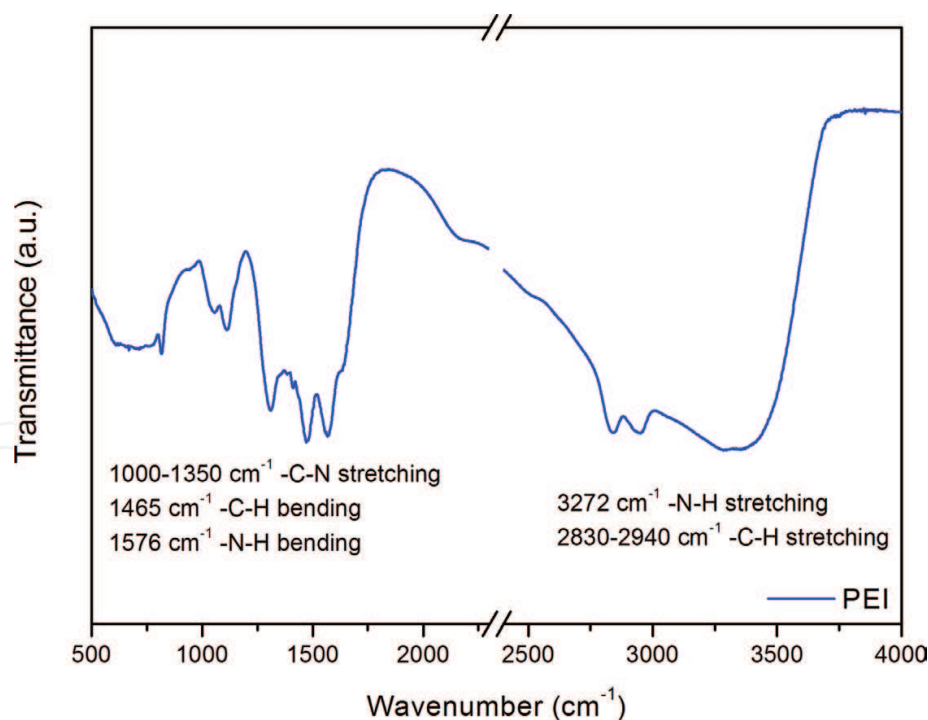


Figure 4. FTIR spectra of the PEI polymer layer deposited at a laser fluence of 0.1 J/cm².

The tests carried out with the SAW sensors showed good performances of the sensors fabricated by MAPLE, in particular the response curve behaviors of the three sensors demonstrated that PIB polymer has a higher sensitivity to DMMP vapor in comparison to PEI and PECH polymers. Therefore, a higher resolution was obtained by using PIB coating.

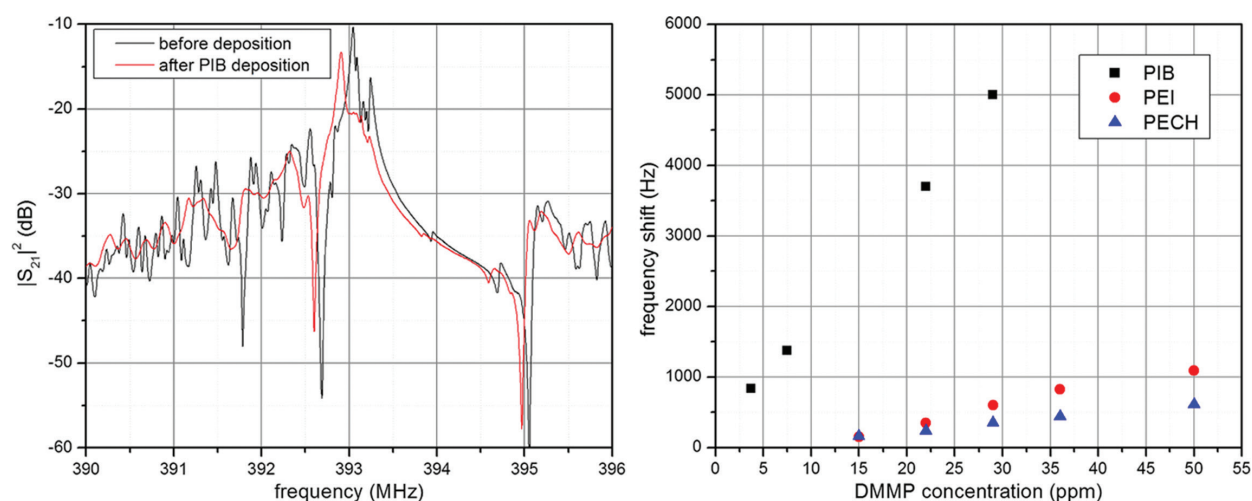


Figure 5. (left) frequency responses of an uncoated SAW sensor and a PIB-coated SAW sensor. (right) PIB-, PEI-, and PECH-coated SAW sensor responses to various concentrations of DMMP (adopted from [21]).

In addition to polymers, proteins and other biomolecules are of great interest in the development of novel sensors and biosensors, and microarray chip devices. Proteins, and in particular odorant-binding proteins (OBPs), show tremendous perspective for integration in devices aimed at the detection of contaminants in food, essential to avoid risks for humans. OBPs are small extracellular proteins which belong to the lipocalin super-family [25, 26]. They have an important role in odor detection by carrying, deactivating, and/or selecting the odorant molecules [27]. In recent studies [28], the possibility of depositing OBPs thin films through MAPLE onto the active area of a SAW device for the development of a biosensor was presented. The sensing system proposed by the authors exploited the high sensitivity and fast response time typical of SAW-based sensors in combination with the adaptable selectivity of the OBPs [29]. The biosensor fabricated in [28] was based on SAW resonators coated through MAPLE with wild-type OBP from bovine (wtbOBP), characterized by different binding specificity, plus an uncoated SAW device used as reference. To demonstrate the functionality of the biosensor, the SAW devices coated by MAPLE were exposed to different concentrations of octanol and carvone, two odorant compounds largely used in the food industry.

The typical coatings of morphology together with the frequency response of the SAW device before and after the MAPLE deposition of wtbOBP (320 mJ/cm² and 46,000 pulses) are shown in **Figure 6a** and **b**. The obtained sensitivities are proportional to the surface density of the wtbOBP coating and, hence, correlated to the laser parameters. Based on the known molecular weight of wtbOBP (37,000 Da) and the frequency shift of 502 kHz (**Figure 6b**) (adapted from [28]), the obtained surface density was found to be 25.86×10^{-6} kg/m², corresponding to 42×10^4 molecules/ μm^2 . In particular, the SAW biosensor showed a higher sensitivity to the carvone odorant (**Figure 6c**, adapted from [28]).

These results demonstrate that MAPLE is a powerful technique to fabricate biosensors with ultimate applications in assessment of food contamination by molds or for the evaluation of indoor air quality in buildings.

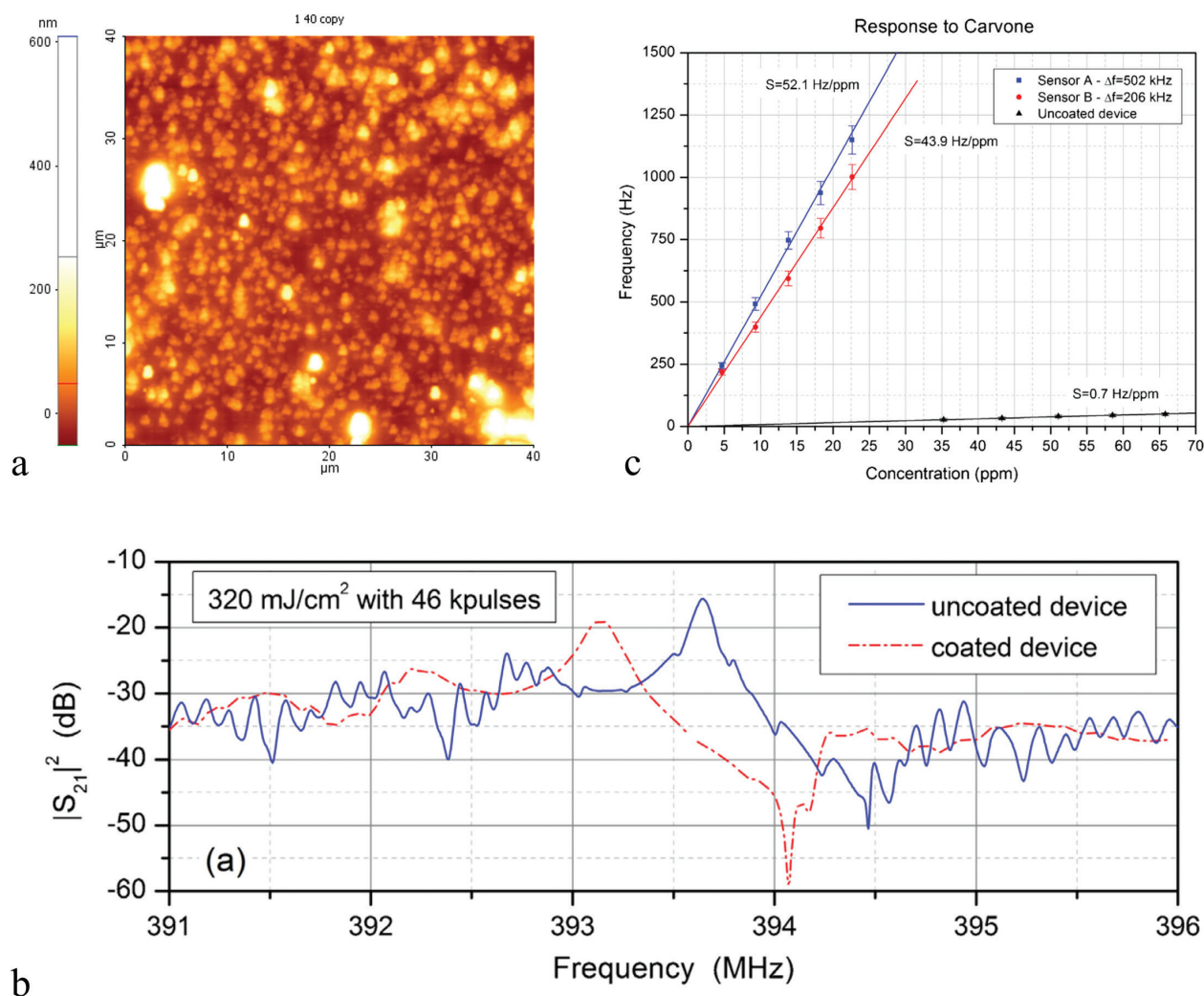


Figure 6. (a) AFM images of wtOBP deposited at 320 mJ/cm² with 46,000 pulses on SAW resonators; (b) the frequency response (amplitude of S_{21}) of SAW devices before and after wtOBP deposition; (c) the response curves for wtOBP-based SAW biosensors and for an uncoated device upon exposure to different concentrations of carvone.

3. Multifunctional active and responsive biointerfaces

Most of the applications related to the biomedical field imply the use of well-controlled biocompatible biointerfaces for medical implants, drug delivery, and lab-on-a-chip devices. Although bulk characteristics of materials are important, due to the direct contact and interaction with the bioenvironment, the surface characteristics, that is, its physical and chemical modification, are directly responsible for its biological outcome and response (e.g., cells ingrowth, protein adsorption, etc.). Therefore, the surface engineering and modifications of the materials used for such applications must take into consideration specific characteristics such as cytocompatibility, mechanical and chemical properties, adhesion with the substrate, controlled morphology and roughness, the feasibility of working with various materials using the same technique, behavior under physiological medium for short and long periods of time, and corrosion.

The ability to deposit or transfer both small and complex, large molecular-mass organic compounds with no or minimum photo-thermal decomposition and preservation of the chemical structure and functionality makes MAPLE an ideal technique to functionalize any type of 2D or 3D surfaces.

It was shown that MAPLE was used not only for obtaining one element coatings (e.g., nanoparticles, proteins, and polymers), but also as a single-step process for various coatings embedding drugs, natural proteins within biodegradable polymeric matrices for bone-related or antitumoral coatings. For example, MAPLE was successfully used for the deposition of hybrid and complex coatings such as multi layers composed of natural and synthetic compounds, for example lactoferrin (Lf), hydroxyapatite nanoparticles (HA), biodegradable polymer (polyethylene glycol-co-polycaprolactone methyl ether (PEG-PCL Me)) [30-34].

Therefore, by combining various specific characteristics of the compounds of interest with the laser parameters in order to tune the interface characteristics of a bio surface, the potential of MAPLE for surface modification and engineering is of crucial importance.

4. Coatings for orthopedic applications

Nowadays, smart devices unifying multiple functionalities, with a high level of integration in a patient body, are the future targets in the medical implant field. The challenges in the medium- and long-term clinical use and performance of orthopedic metallic implants are considering the tailoring and improvement of traditional implant engineering materials, and are related to stable anchorage in the bone tissue by rapid osseointegration and low inflammatory response. Therefore, multifunctional hybrid smart coatings having bone-matching properties, combined osseo-inductive, osseo-conductive and infection-preventing abilities, low inflammatory response as well as highly adhesion on the substrate surface and flexibility in tailoring the composition, appropriate surface chemistry, and architecture are highly desirable.

MAPLE is crucial for the realization of joining process between metallic alloy substrate and the biomimetic coatings as it confers high adhesion, thickness, and morphology control. Obtaining of optimal performance of the multifunctional biomimetic coatings (bioactive layers mimicking the bone bio mineralization process and which jointly mimic the biological osseo-integration processes, bone bonding, and prevent infections, having a controlled release of bioactive factor) was approached by combining the specific properties of the different compounds:

- Biodegradable and bioresorbable copolymer PEG-PCL-Me, as multifunctional coating and matrix for embedding bioactive factor, is mainly used as protein repellent; bone bonding

polymer for better adhesion to metallic implant substrate; matrix for entrapping and controlled release of bone induction factors/bioactive factors.

- HA for osteogenic potential and for improving mechanical properties of the coating;
- Lactoferrin, as natural protein with antibacterial properties and rich chemistry for minimizing host inflammatory reactivity. In addition, it can be used as bone induction regulator, maintenance, and repair and for further binding of active factors and as bone growth factor by promoting proliferation, differentiation, and survival of osteoblasts.

Although the mentioned materials have distinctive chemistry and characteristics, the realization of joins between them, as heterostructures or composites and hybrids, is possible by applying a modified MAPLE technique as shown in **Figure 7**.

The high potential of the MAPLE technique in embedding multiple bioactive factors, into a biodegradable synthetic polymeric thin film (PEG-PCL Me) in a single step and under vacuum conditions, with minimum influence of solvents or deposition conditions on the functionality of Lf or HA, is the main reason for choosing it as flexible method for a controlled functionalization of implant surface in terms of quality, quantity, and morphology for promoting survival, proliferation, and differentiation of murine MC3T3-E1 pre-osteoblasts. The initial attachment of cells to the biomaterial is dependent on surface properties, and detectable changes in cell shape and cytoskeleton organization were remarked, as shown in **Figure 8** (after 2 h) and **Figure 9** (after 24 h).

In vitro biological assessment of all analyzed biomaterials indicated that they differentially promoted cell adhesion and proliferation and supported different degrees of extracellular matrix mineralization with improved initial bioresponse for the PEG-PCL-Me-HA.

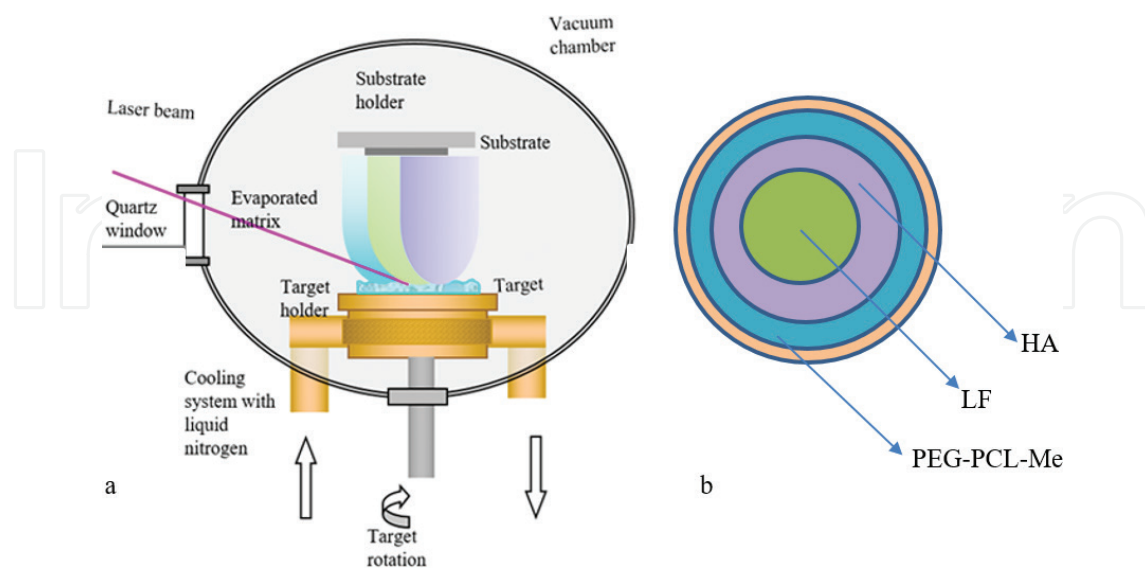


Figure 7. Experimental setup (a) and target modification (b) from [34].

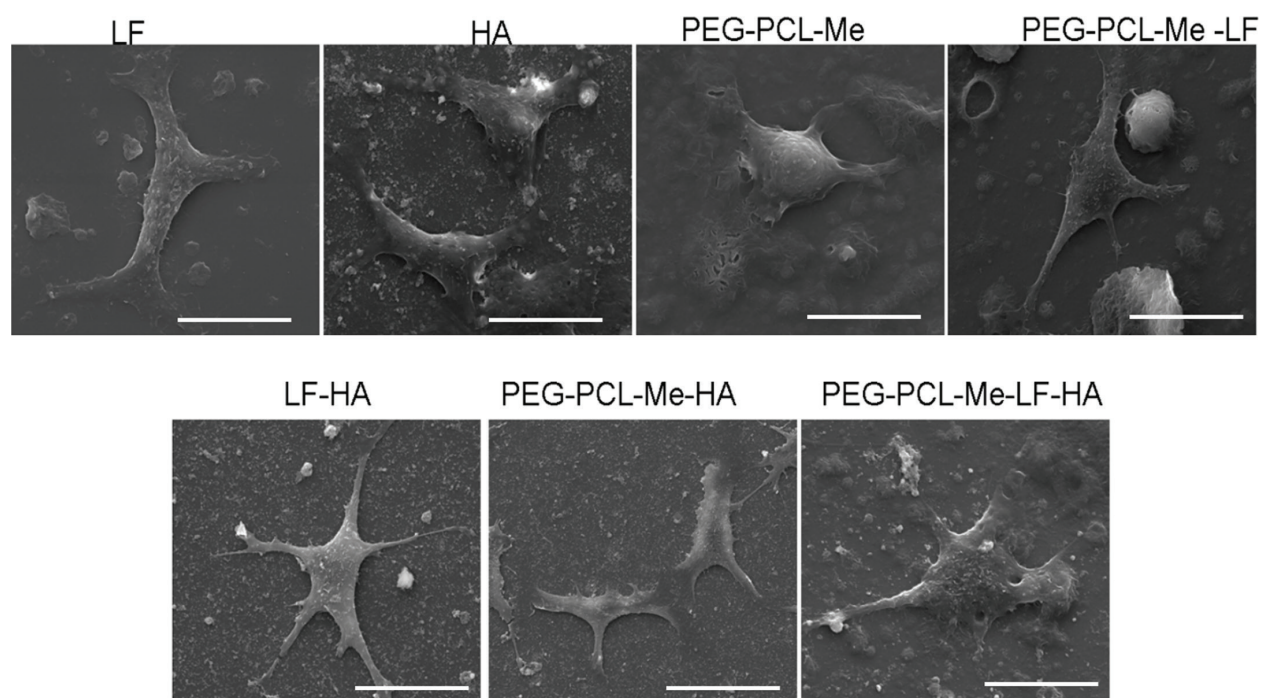


Figure 8. Early biological response of MC3T3-E1 cells to the analyzed biomaterials: The ability of pre-osteoblasts to adhere on the analyzed substrates after 2 h of culture. Scale bar is 20 μm in all images.

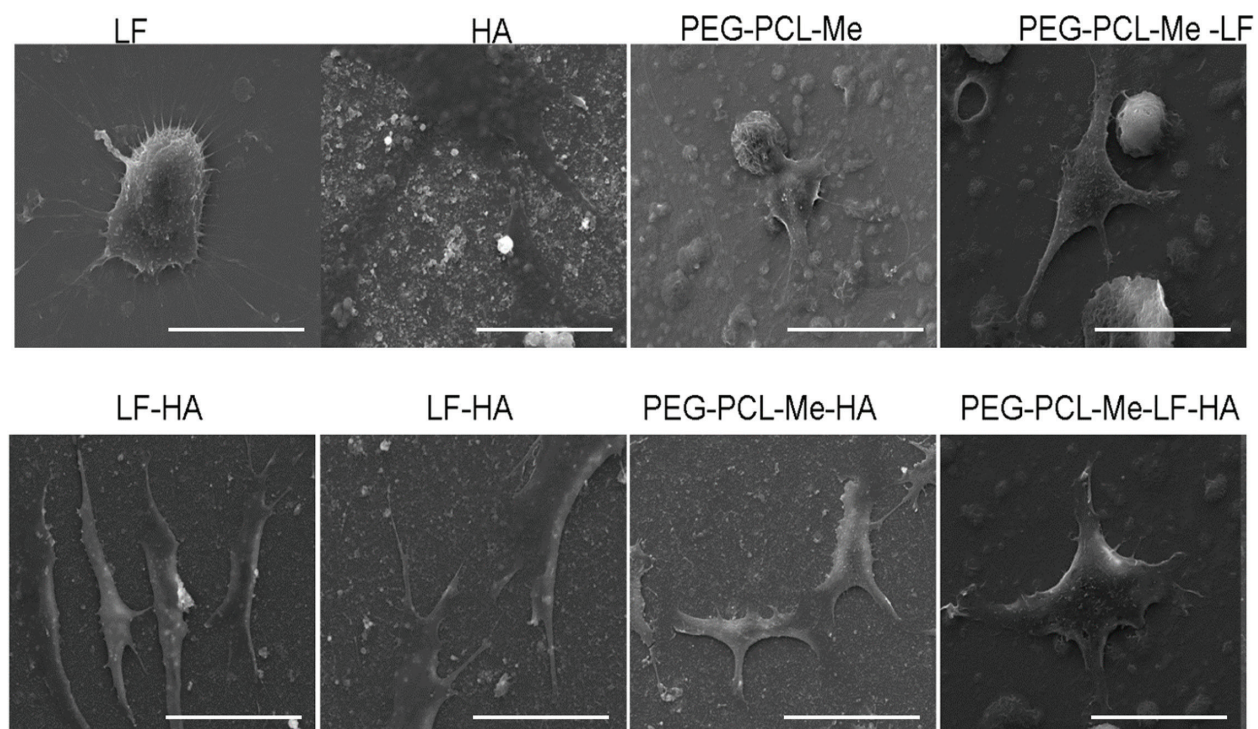


Figure 9. Cellular morphological features at 24 h post-seeding. Scale bar is 20 μm in all images.

5. Biodegradable and non-biodegradable coatings as antitumoral systems

The use of bio platforms for the short- and long-term study of the cancer cells exposed to various drugs represents one research direction of interest. Given the fact that tumoral cell lines

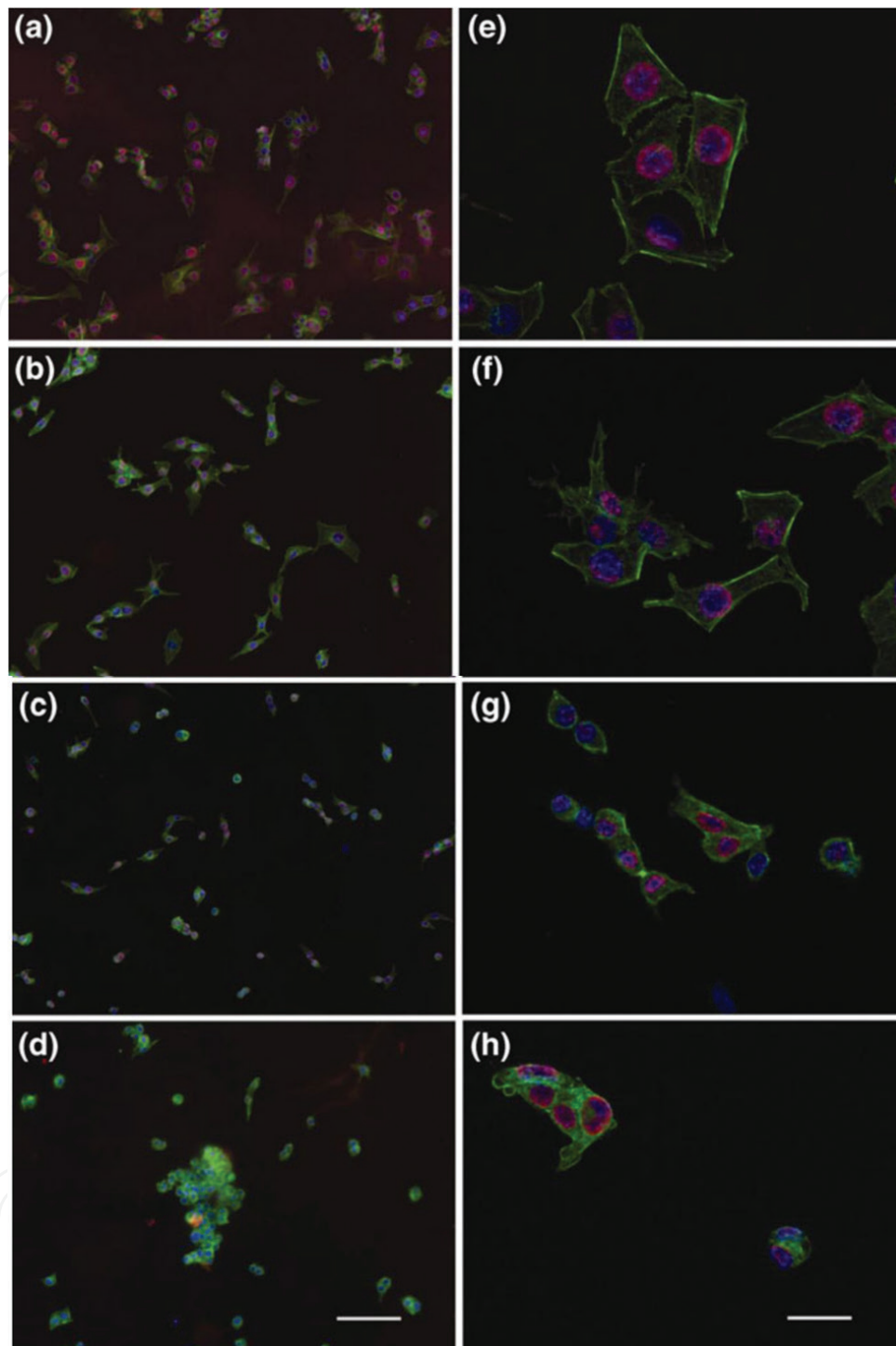


Figure 10. Proliferation and adhesion of B16-F10 melanoma cells after 24 h, onto different substrates: PCL (a, e), PCL_Cis (b, f), PCL_Apo-rLf (c, g), and PCL_Apo-rLf_Cis (d, h). Immune-fluorescence microscopy reveals Ki67 for proliferation and actin filaments for adhesion. Scale bar is 200 μm (a–d) and 50 μm (e–h). (adopted from [28].).

such as malignant melanoma are resistant to most of the chemotherapeutic agents, finding an optimal solution by synergetic effect of drugs with natural proteins is a requirement. In addition to resistance to the chemotherapeutic effect, drugs such as cisplatin (Cis) can induce a nephrotoxic effect on cells. By using both recombinant iron-free lactoferrin [(Apo-rLf)] and Cis embedded within a biodegradable polycaprolactone coating, the effect on the murine melanoma B16-F10 cells' morphology and proliferation was investigated revealing a decreased

viability and proliferation, in the case of melanoma cells cultured on both Apo-rLf and Cis thin films (**Figure 10**).

Furthermore, since its initial synthesis, the temperature-responsive surfaces of poly (N-isopropylacrylamide) (pNIPAM) were studied for biomedical applications related to sensors, drug delivery, or tissue engineering applications [35, 36].

For example, MAPLE was used to demonstrate that pNIPAM coatings could be tailored in terms of thickness and roughness as thermo-responsive surfaces for L929 fibroblast cell line adhesion and single-cell detachment studies. It was found that the cells did not change their shape or viability, indicating that the control of cell attachment-detachment by changing temperature is a reversible and reproducible process [37].

By combining pNIPAM with dacarbazine drug, the effect on HT29 tumoral cell line was evaluated. There were no restraining in cell development on the PNIPAM coatings while embedding dacarbazine led to significant changes in both cellular numbers and shape **Figures 11** and **12**.

By laser surface engineering and/or functionalization, a wide range of structural, chemical, and morphological characteristics could be achieved, with optimization steps applied

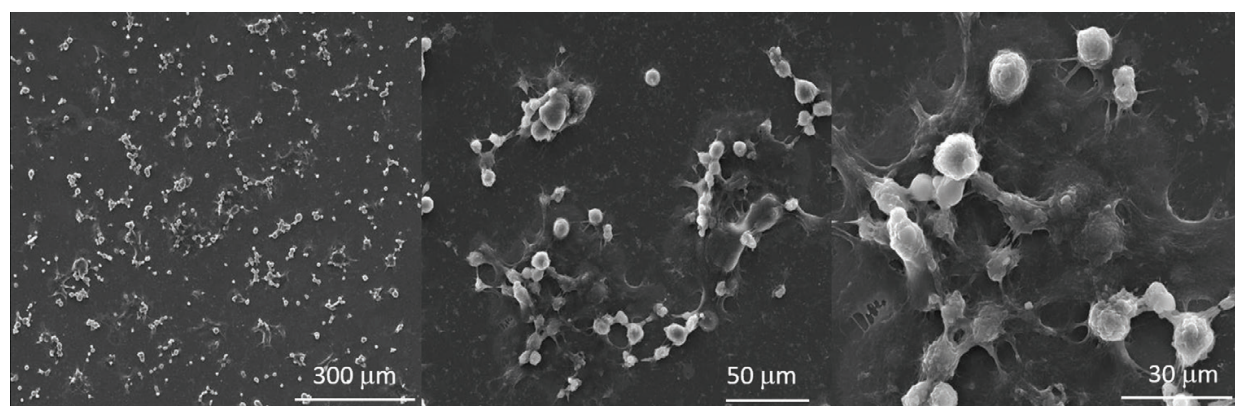


Figure 11. SEM images of HT29 cells onto the pNIPAM coatings obtained by MAPLE at 36,000 pulses and 400 mJ/cm² laser fluence.

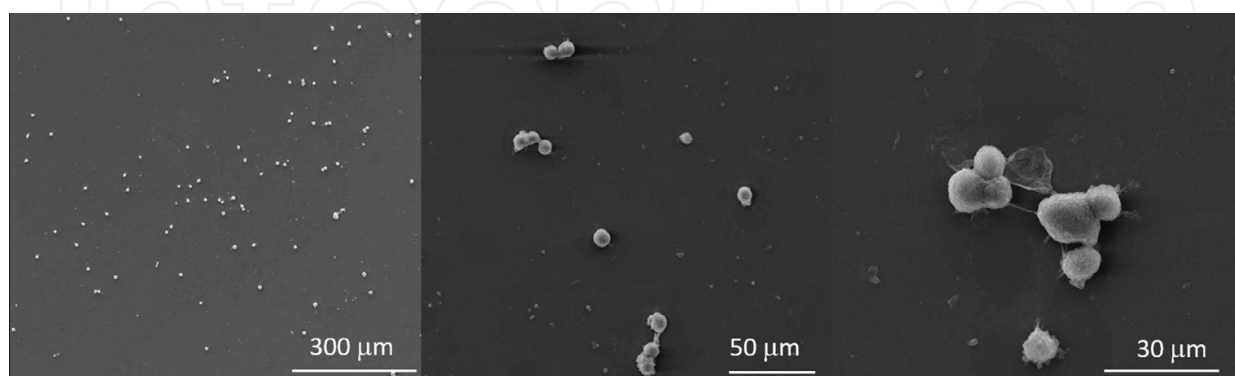


Figure 12. SEM images of HT29 cells onto the pNIPAM-dacarbazine coatings obtained by MAPLE at 36,000 pulses and 400 mJ/cm² laser fluence.

accordingly to the specific application. Therefore, a scientific interdisciplinary approach involving the “synthesis” of new materials, analysis, and correlation of the materials bulk and interface characteristics to its bioenvironment represents a method to tackle the future of bioengineering.

6. Conclusions

This chapter summarizes some applications and developments in the field of matrix-assisted pulsed laser evaporation (MAPLE) of polymers and biomolecules, that is, protein thin film deposition. The data shown suggest that MAPLE is a promising approach for depositing proteins (lactoferrin, odorant-binding proteins) and polymers (polyisobutylene, polyethylenimine, and polyepichlorohydrin) as thin films that can be utilized for the fabrication of novel biosensors, or smart devices with multiple functionalities. Furthermore, one might combine different specific characteristics of the compounds of interest with the laser processing parameters, and is therefore being able to tune the interface characteristics of a bio surface, thus enhancing the potential of MAPLE for surface modification and engineering.

In addition, it has been shown that the deposition process of the polymer and protein materials can be optimized by modifying the process parameters, that is, laser wavelength, laser fluence, active material concentration in the target, etc. Considering the above-mentioned advantages of the MAPLE technique on depositing materials with very high reproducibility, one could envision that this approach could provide a new strategy to engineer and/or functionalize new materials to be used for regenerative biomedicine, tissue engineering studies, medical implants, or biosensors. Conflict of interest The authors declare no competing interests.

Acknowledgements

Financial support from the Romanian Nucleus Program: contract 4 N/2016 and from the Romanian National Authority for Scientific Research, CNCS: UEFISCDI project number PN-II-PT-PCCA-2013-4-1992 (SOLE), PN-II-PT-PCCA-2013-4-1870 (ARCOLAS), PN-II-PT-PCCA-2013-4:199 (ORTHOBIMIM), PN-II-RU-TE-2014-4-2334, and PN-II-RU-TE-2014-4-2311 (FLEXSENS), is gratefully acknowledged.

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