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Abstract

The deposition of hydroxyapatite thin films has become a topic of interest in medical applications. This dental film applied on the surface of the tooth may act as a highly resistant and flexible artificial enamel, protecting teeth and removing tooth sensitivity. Other possibilities include whitening and coating enamel-deficient structures. We obtained this flexible film of hydroxyapatite using laser ablation. The plasma plumes were generated by an Nd:YAG nanosecond laser in a vacuum chamber. We used the pulsed laser deposition (PLD) technique and conducted investigations using optical emission spectroscopy (OES), laser-induced breakdown spectroscopy (LIBS), and Raman spectroscopy. Initially, a thin film of HA was deposited on a soluble substrate and heated, followed by immersion into pure water to dissolve the substrates. The originality of our approach consists in the fact that the flexible HA film can be obtained in pure state, because it grows without a substrate, using just a base and lateral supports between, on which it will grow vertically. In order to verify the compatibility and the “stickiness” of HA on the teeth, we chose to grow the film between the roots of a tooth. In this case, besides the film, we also obtained HA microfibers. We tried to bind the film on an extracted tooth. A protocol must be established in order to allow the bonding of the film to the surface of the tooth, knowing that contaminants such as saliva or sulcular fluid increase bonding strength to enamel or dentin. We realized an efficient bonding as HA absorbs protein, the mineral also participates in this ionic exchange, and we strengthened the tooth structure. The main purpose of our research is to rebuild the dentine layer or enamel and close the dental channels. Our experiments led to the creation of an HA foil that has the role of protecting teeth against cariogenic bacteria and could even have cosmetic effects by teeth whitening. This dental plaster acts as an artificial HA enamel, very resistant and flexible, protecting the tooth and eliminating...
1. Introduction

This chapter describes a unique way to obtain a flexible pure hydroxyapatite film. In the past years, the nanocomposites have been in the center of attention due to their unique physical and chemical properties.

Specifically, the biomaterials have been widely studied, motivated by their clinical applications. Among these, the hydroxyapatite has been studied due to its remarkable properties, such as biocompatibility, osteoconductivity, and bioactivity. This material is naturally found in the human body, being one of the major constituents of bones and teeth. As a consequence, HA has been widely used in many fields, including biomedical applications. Our experiments led to the creation of a thin HA film that has the role of protecting teeth against cariogenic bacteria and could even have cosmetic effects by teeth whitening. This dental plaster acts as an artificial HA enamel, very resistant and flexible, protecting the tooth and eliminating dental sensitivity. Being very thin, it is invisible once applied on teeth and can be observed only by examination under a strong light. The plaster, produced by pulsed laser deposition (PLD), can be manipulated with tweezers and applied on the tooth. The originality of our approach consists in the fact that the flexible HA film can be obtained in pure state, because it grows without a substrate, using just a base and lateral supports between which it will grow on vertical direction.

2. Experimental methods

The deposition of hydroxyapatite thin films has become a topic of interest in medical applications. This dental film applied on the surface of the tooth may act as an artificial, highly resistant, and flexible enamel, protecting teeth and removing tooth sensitivity. There is also a possibility for whitening and covering deficient enamel structure. We obtained this flexible film of hydroxyapatite using laser ablation. We also tried to apply the film on an extracted tooth. The plasma plumes were generated by an Nd:YAG nanosecond laser in a vacuum chamber with $10^{-6}$ Torr. We used the pulsed laser deposition technique and for the investigations we opted for optical emission spectroscopy (OES) and Raman spectroscopy.

In this work, we studied the evolution of plasma plumes resulting from enamel and hydroxyapatite ablation. The plasma plumes were generated by an Nd:YAG nanosecond laser and the depositions were performed in a cylindrical stainless steel vacuum chamber (10 L volume, 30 cm height, 20 cm diameter) (Figure 1). The chamber is evacuated to a base pressure...
of 10⁻⁶ Torr by a 550 L/s turbomolecular pump (Agilent Technologies TV-551) placed in a vertical position at the bottom of chamber. The target (HA) is placed on a micrometric precision XYZ stage and can be rotated with a motorized vacuum feedthrough (Caburn MDC). The target is placed on a metallic target holder, which is electrically isolated from the rest of the experiment by an alumina block. The substrate (salt) is placed parallel to the target. The target-substrate distance was 1.4 cm. The ablation laser beam was usually at 45° on the target surface (Figure 2).

![Vacuum chamber](image1)

**Figure 1.** Vacuum chamber.

![Experimental setup](image2)

**Figure 2.** Experimental setup of an Nd:YAG nanosecond laser (Continuum Surelite III-10) (gw = 1 μs, gd = 25 ns).
2.1. Experimental data

We used $\lambda = 266$ nm, 10 ns, 10 Hz, $E = 40$ mJ/pulse, fluence 2.1 J/cm$^2$. The materials used in these studies were hydroxyapatite and a human tooth (Figure 3a–d).

2.2. Results and discussions

The dynamics of the plasma plume has been studied by means of a high-resolution monochromator (Acton SP 2500i) and intensified charge-coupled device (ICCD) camera (Roper Scientific PI MAX2-1003-UNIGEN2, 1024 × 1024 pixels). The monochromator has an alternative exit port fitted with a photomultiplier (PM, Hamamatsu) in order to record fast temporal profiles of a given spectral line. The PM output is sent to a fast digital oscilloscope (GHz, LeCroy). In order to obtain preliminary insight into the dynamics of the laser ablation plasma plume, ICCD sequential pictures of the spectrally unresolved plasma optical emission were recorded at various delays with respect to the laser pulse. We used the PLD technique to produce flexible films of hydroxyapatite deposited on glass or NaCl (salt) substrates, followed by a space-and-time-resolved optical emission spectroscopy (OES) investigation on selected spectral lines, the properties of the deposited films were investigated by Raman spectroscopy.

We used the ICCD camera to record the global template evolution of the plasma (Figure 4) and we observed the presence of two main structures: a fast one, represented by the spectral lines of ions, and a slower one, mainly due to the contribution of neutrals (the first one, plume-like-shaped, expands at a velocity of about $2 \times 10^4$ m/s; the second one, which looks like a small plasma cloud close to the target surface, shows an expansion velocity of about $2 \times 10^3$ m/s). OES allowed us to obtain information on the contribution of each species present in the plasma, the processes of formation and expansion of the plume. Identification of spectral lines observed in the OES was performed using the NIST database and CFA (Figure 5).
Emission is dominated by Ca I, Ca II ions but O II, H I, and contaminants such as Na I, Mg III, Hg I ions were also found. Raman analysis of HA deposition on glass and Raman analysis of HA deposition on salt are presented in Figures 6 and 7, respectively.

Figure 5. OES hydroxyapatite/OES enamel tooth.
A starting point in the investigation of the thin HA film is to obtain information on the surface morphology of the deposited samples. For the study of the thin film discussed here, we used a confocal optical microscope (Olympus) coupled to the Raman spectroscopy setup (Renishaw). Our images were obtained using the 50× objective (Figure 8).
A thin film of Hap was deposited on a soluble substrate by a pulsed laser deposition (PLD) technique. The substrates were then dissolved using a solvent and the thin Hap films were collected as freestanding sheets. The HA film was deposited on salt single crystals (Figure 9) and heated at 400°C, \( t = 30 \) min. These HA sheets were crystallized. Thereafter, the thin films were collected as freestanding sheets by immersing the NaCl substrates into pure water to dissolve the substrates. This procedure gave rise to flexible HA films.
Laser-induced breakdown spectroscopy (LIBS) uses a short laser pulse (≈10 ns) focused on the surface of a solid sample to vaporize a very small quantity of material. The ejected material forms a plasma plume and the optical radiation emitted by the plasma species is collected through an optical fiber exactly where the plasma was produced, meaning that this method can be used for *in situ* analysis. Because the quantity of ejected material is in the order of 20–200 ng, this method is considered microdestructive because the crater formed on the surface of the sample is practically invisible to the naked eye. LIBS can be used for elemental analysis of materials and it allows the measurement of fluorescence lifetime of the species identified in the plasma. For the LIBS analysis, we used the third harmonic of an Nd:YAG (BMI LT-1233) laser (355 nm, 10 ns) focused by a 5 cm focal distance lens. The optical radiation emitted by the plasma plume was collected using an optical fiber and analyzed using a monochromator and detected with a photomultiplier (H9305-02 Hamamatsi) connected to a 500 MHz oscilloscope (Agilent Technologies) (Figure 10). This way, we were able to measure the intensity of the radiation emitted at various wavelengths and to record the time evolution of each signal.

The measurements have been performed at IESL-FORTH (Institute of Electronic Structure and Laser-Foundation for Research and Technology-Hellas), Greece. The HA pellet was placed 1 cm before the focal point in order to avoid laser focusing in the air and air breakdown. The laser fluence could be adjusted by changing the area of the laser spot at the surface of the sample by modifying the lens-sample distance. Experiments were performed at 1.47 J/cm² (fluence) \( (E = 7.4 \text{ mJ}, 10 \text{ Hz}, D = 0.8 \text{ mm}, S = 0.50 \text{ mm}^2) \).

The main species identified are Ca I, then HI and OII, but also the main contaminant, Na I. The fluorescence lifetime of Ca I and oxygen is considerably larger (Figure 11).

### 2.3. Vertical growth methods for flexible HA films

In order to obtain flexible HA films, we used PLD starting from a solid pure HA pellet as a target. The powdered HA was processed in the form of solid pellets of 14–15 mm diameter and 4–6 mm thickness using a hydraulic press (15–25 tones) at “Gheorghe Asachi” Technical University of Iasi (Figure 12).
The hydroxyapatite thin films were obtained by nanosecond PLD. This method proved to be competitive for growing high-quality thin films because it has the capacity to preserve the stoichiometry of deposed compounds [4]. Obtaining thin films using PLD offers many advantages compared with other techniques, such as the laser source is external to the deposition chamber, most materials can be laser ablated and deposed in thin films, and the growth rate can be precisely controlled ($10^{-2}$ to $10^{-1}$ nm/pulse); the ablated material is localized in the volume of the generated plasma; the stoichiometry of the film is identical with that of the target and the high energy of ablated species allows one to obtain very adherent films [5–8]. The film depositions were performed using an Nd:YAG laser, BMI Industries, at IESL-FORTH (Institute of Electronic Structure and Laser-Foundation for Research and Technology-Hellas, Heraklion) Greece, at $\lambda = 266$ nm, repetition rate 10 Hz (Figure 13). Various fluencies were used and the target substrate distance was also adjustable (Table 1). As previously explained, the fluence can be varied by changing the distance between the focusing lens and the target surface.
Table 1. Laser fluence.

| Diameter (mm) | Area (mm²) | Area (cm²) | Measured power (mW) | Repetition rate (Hz) | Energy (mJ) | Fluence (mJ/cm²) | Fluence (J/cm²) |
|--------------|------------|------------|---------------------|----------------------|-------------|------------------|-----------------|
| 0.8          | 0.502655   | 0.005027   | 74                  | 10                   | 7.4         | 1472.183         | 1.472183        |
| 1            | 0.785398   | 0.007854   | 66                  | 10                   | 6.6         | 840.3381         | 0.840338        |
| 1.5          | 1.767146   | 0.017671   | 200                 | 10                   | 20          | 1131.768         | 1.131768        |

Figure 13. PLD experimental setup.

Figure 14. HA ablation plasma/HA vertical film obtained on salt substrate.
Figure 15. HA film formed between two lateral supports/vertical HA film attached only at the base.

Figure 16. HA microfibers attached to the tooth surface.

Figure 17. Optical microscope 15×, Brunel microscopes.
Initially, we made a deposition on a salt (NaCl) substrate and it led to the formation of some HA vertical structures (Figure 14). The next step was to obtain films that were not completely attached to the substrate by growing them between two lateral supports. In order to verify the compatibility and the “sticking” of HA on the teeth as well, which corresponds to the intended application, we chose to grow the film between the roots of a tooth (Figure 15). In this case, besides the film, we also obtained HA microfibers attached only at one end on the tooth enamel (Figure 16). We used for these experiment Optical microscope (Figure 17).

In order to improve the crystallinity and biocompatibility of the films, they were thermally treated for 30 min at 400°C (Figures 18 and 19).

2.4. Methods of HA adhesion on enamel

This flexible HA film can be handled with tweezers and applied to the tooth. We tried to bind the film on an extracted tooth.
Adhesion to enamel is the hard process (Figure 20). A protocol must be established in order to allow the bonding of the film on the surface of the tooth knowing that contaminants such as saliva or sulcular fluid increase bonding strength to enamel or dentin. We realized an efficient bonding as HA absorbs protein, the mineral also participates in this ionic exchange and we strengthened the tooth structure.

Using the PLD technique, we can obtain a flexible film of hydroxyapatite, a biocompatible dental material that can be immediately and directly attached to the tooth surface for restoration and conservation of teeth.

For the experimental part, we have attached a theoretical model [8–16].

We proposed a new approach for the analysis of dynamics in nanostructures. The dynamics of nanostructure quasiparticles takes place on continuous but nondifferentiable curves. Consequently, the standard properties of nanostructures, such as quasiparticles generation through self-structuring, interferential capacities through self-similar solutions of Kirchhoff type equations, etc., are controlled through nondifferentiability of motion curves.

The standard theoretical models of nanostructures dynamics are sophisticated and ambiguous. However, such situation can be simplified if we consider that complexities in interaction processes impose various time resolution scales and the evolution pattern leads to different freedom degrees. To develop new theoretical models, we have to admit that the nanostructures with chaotic behaviors can achieve self-similarity (space-time structures can appear) associated with strong fluctuations at all possible space-time scales. Then, for time scales that prove to be larger if compared with the inverse of the highest Lyapunov exponent, the deterministic trajectories are replaced by a collection of potential routes. In its turn, the concept of “definite positions” is replaced by that of probability density.

Thus, the nondifferentiability appears as a universal property of nanostructures and, moreover, it is necessary to create nondifferentiable physics of nanostructures. Under such circumstances, if we consider that the complexity of interactions in the dynamics of nanostructures is replaced by nondifferentiability, it is no longer necessary to use the whole classical “arsenal” of quantities from standard physics (differentiable physics).

This topic was developed using either the scale relativity theory (SRT) or scale relativity theory with arbitrary constant fractal dimension. According to these models, the dynamics of
Various theoretical aspects of nanostructure dynamics (self-structuring, phenomena through quasiparticles generation, interferential capacities through self-similar solutions of Kirchhoff type equations, etc.) were analyzed using the SRT with arbitrary constant fractal dimension.

Any particle can take part in a permanent interaction with the “subfractal level” through the fractal potential, $Q$. The “subfractal level” is identified with a nonrelativistic fractal fluid described by momentum and state density conservation laws. The nondifferentiable hydrodynamics implies a quantum hydrodynamics model (QHM). Indeed, for motions described by fractal curves with fractal dimension $D_F = 2$, at Compton scale, the Non-differentiable hydrodynamics (NDH) reduces to quantum hydrodynamics model. Moreover, the “subfractal level” can be identified with “subquantum level.” The fractal potential comes from the nondifferentiability and must be considered as a kinetic term and not as a potential one. Moreover, the fractal potential can generate a viscosity stress tensor type.

The main conclusions of the theoretical model are the following: (i) the nanostructure dynamics was theoretically analyzed assuming that the quasiparticle moves on continuous and nondifferentiable curves; (ii) a nondifferentiable hydrodynamic model containing the density and momentum conservation equations was built. The fractality is introduced via fractal potential; (iii) supposing that the fractal potential implies an isentropic-type behavior of the fractal fluid, the self-structuring phenomena are analyzed through numerical simulations; (iv) in the absence of convection, interferential properties are induced in nanostructures; (v) this chapter deals with the standard properties of nanostructures, such as quasiparticles generation through self-structuring or interferential capacities through self-similar solutions of Kirchhoff-type equations. In the literature, there are also other descriptions of the forms of organization of the matter. The quantum theory is used in each of these descriptions of the forms of organization of matter. However, the interpretation of modern quantum theory is still an open question as shown in the Reference [1–3].

3. Conclusions

We created a flexible HA film, a dental plaster grown vertically, thus improving its quality: there are no contaminations and impurities from the substrate. The crystalline structure can be improved by thermal treatment. The main purpose of our research is to rebuild the dentine layer or enamel and close the dental channels.
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