

Studying nucleation kinetics of bioceramics

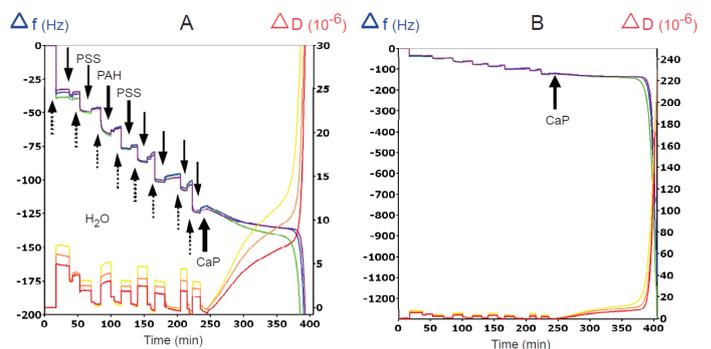
Bioceramic coatings of calcium phosphate (CaP) are used to improve the biological properties of medical implants. The crystallization of CaP is initiated on polyelectrolyte multilayers (PEMs). PEMs are used to build up well-defined surfaces and by modifying the multilayer, the crystal nucleation and growth of CaP can be controlled. PEMs are used in many biomaterial applications thanks to the ability to create surface coatings with desirable properties. They can also be modified to release drugs or active peptides. Here we show how QCM-D is used to optimize the process thanks to the unique possibility to monitor the build up and viscoelastic properties of the multilayer as well as the nucleation kinetics and crystal growth of CaP in situ in real-time.

Quartz Crystal Microbalance with Dissipation is an acoustic surface sensitive technique, which provides simultaneous, real-time information on mass and structure of thin films. The mass of an adsorbed adlayer is sensed as resonance frequency of the sensor movement (Δf) and the viscoelastic properties are deduced from the damping of the sensor movement (ΔD). In this application, these parameters give real-time information about the buildup and viscoelasticity of the polyelectrolyte multilayer, as well as the nucleation kinetics of calcium phosphate crystal growth.

Background

In order to enhance implant fixation, biological properties of implanted materials are improved by calcium phosphate (CaP) bioceramic coatings as a bioactive interface between the bulk metal implant and the surrounding tissue. Their close resemblance to the chemical and mineral components of teeth and bone make them biocompatible and prone to integrate with bone.

The first CaP coatings were produced via vapour phase processes, but more recently solution-based and biomimetic methods have emerged. The solution-based procedure requires an underlying surface that promotes the growth of crystals in a controlled manner. Polyelectrolyte multilayers have been found useful since by modifying the polyelectrolytes and the multilayer assembly process, the nucleation lag time and growth of crystals can be controlled¹. Generally, polyelectrolyte multilayers are used in many biomaterial applications due to the unique possibilities to create surface coatings with desirable properties.



[Figure 1]: CaP mineralization on a polyelectrolyte multilayer was followed by QCM-D. (A) a polyelectrolyte multilayer is formed by the deposition of PEI to the gold surface and followed by alternate exposure to PSS (4') and PAH (3'). Polyelectrolyte exposures and rinses with water are indicated by solid and dotted arrows, respectively. (B) 5 mM CaP is exposed to the washed multilayer (thick solid arrow). After a lag time of more than 100 min after the CaP addition, crystal growth is evidenced by the strong changes in f and D . Figure A is a close up of figure B, notice the different scale on the y-axis.

Approach

Polyelectrolyte multilayers were constructed in situ by alternate adsorption of poly(styrene sulfonate) (PSS) and polyallylamine (PAH) onto Q-sense gold sensors, pre-modified with a layer of poly(ethyleneimine) (PEI). Supersaturated CaP solutions were injected onto the polyelectrolyte multilayer surface in situ and the heterogeneous nucleation of CaP crystals was studied in real-time. Parameters such as multilayer build-up procedure, CaP concentration and temperature were varied.

Results and discussion

Figure 1 shows the deposition of the polyelectrolyte multilayer and subsequent addition of CaP solution, in this case a 5 mM CaP solution in contact with a multilayer that ends with a polyanionic layer of PSS. Figure 1A shows a close-up of the multilayer deposition and how the mass increased after each deposition. The crystal growth started after a lag time of more than 100 minutes from the injection of CaP solution. Figure 1B shows the sharp and large shift in frequency and dissipation due to the rapid growth of CaP crystals at the end of the measurement.

The QCM-D experiments showed clear evidence of the two main steps of CaP mineralization: (i) lag time for nucleation and (ii) crystal growth, after a characteristic induction time that depended on the solution composition and surface properties. This confirms and completes results obtained with an optical technique².

Conclusion

By performing studies of the kinetics of CaP mineralization at differently modified surfaces, the QCM-D technique reveals itself as a powerful real-time tool to provide information about biomineralization mechanisms and their control at solid interfaces.

References:

This application note is based on work by G. Ladam, A. Johansson and H. Atmani from the Laboratoire de Biophysique et Biomatériaux (La2B), Université de Rouen, Evreux, France.

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2. Ngankam et al. "Influence of polyelectrolyte multilayer films on calcium phosphate nucleation" *J. Am. Chem. Soc.* 2000, 37, 8998.



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