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Functionalization of Semicrystalline Hydroxyapatite Coatings with Citrate as New Approach in Orthopaedic Applications

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INTRODUCTION & AIM

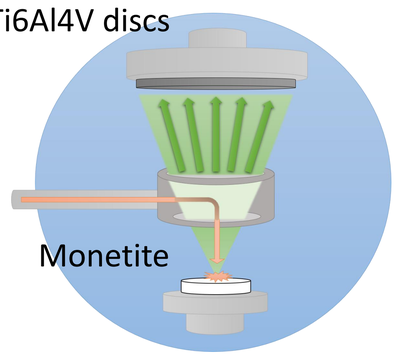
Hydroxyapatite (HA)-based nanocoatings are used in orthopedics to promote osseointegration due to their chemical similarity to the mineral component of human bone. The application of calcium phosphate (CaP) coating onto titanium alloy prosthesis surface can favor osseo-integration process with host bone tissue and avoid the mobilization of the implant. The incorporation and functionalization of these coatings with citrate can enhance tissue mineralization, as citrate plays a key role in the activity of osteogenic cells and in stabilizing the bone matrix and represent 1-2% of total bone tissue.

Here, semicrystalline HA coatings were fabricated using two different deposition techniques: Ionized Jet Deposition (IJD) and biomimetic deposition by simulated body fluid (SBF). The use of thermal treatment after deposition onto coating properties was explored. Subsequently, they were loaded via citrate adsorption to identify which coating was more adequate for combination with citrate.

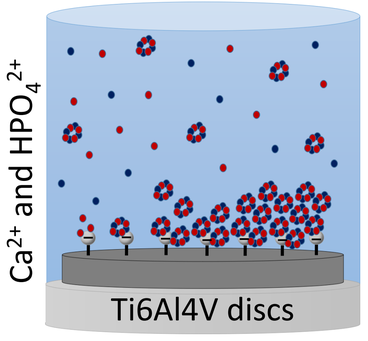
MATERIALS & METHODS

Physical Deposition: IJD

Ti6Al4V discs

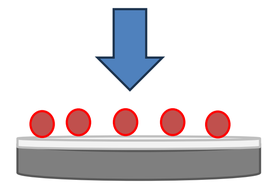


Chemical Deposition: Biomimetic Deposition by SBF



Functionalization with citrate: via absorption

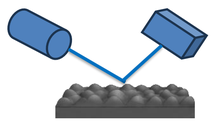
Citrate concentration: 1, 10 and 50 mM
Incubation for 6h at 37°C



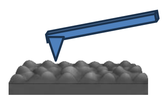
Ti6Al4V discs coated with semicrystalline HA

Coating were deposit at room temperature (RT) and were thermically treated at 400°C (TT)

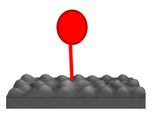
Coating characterization



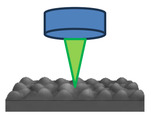
X-Ray Diffraction (XRD)



Atomic Force Microscopy (AFM)



FTIR Spectroscopy

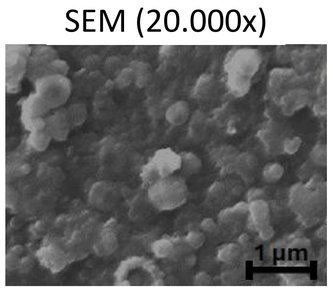


Scanning Electron Microscopy (SEM)

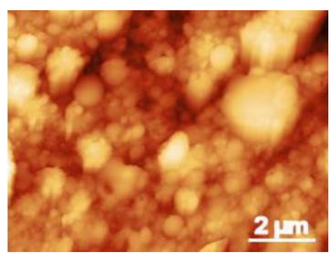
RESULTS & DISCUSSION

Physical Deposition: IJD

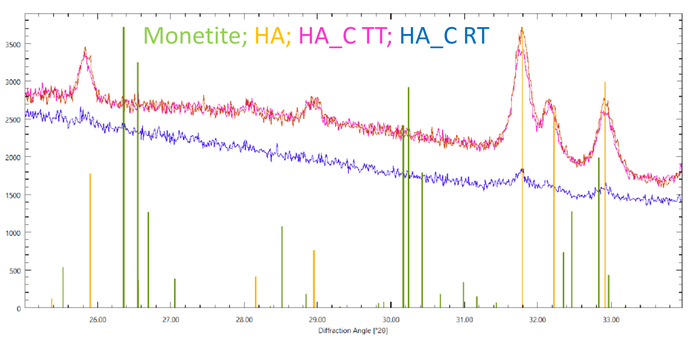
SEM (20.000x)



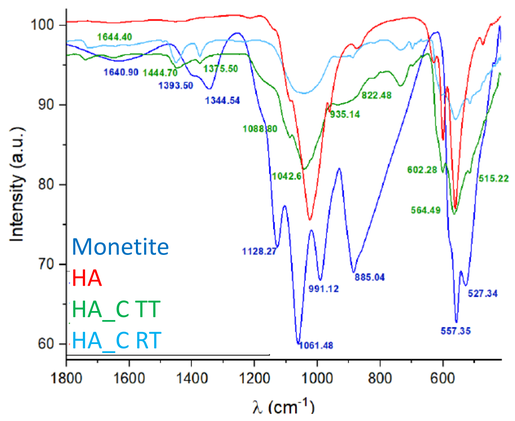
AFM



XRD



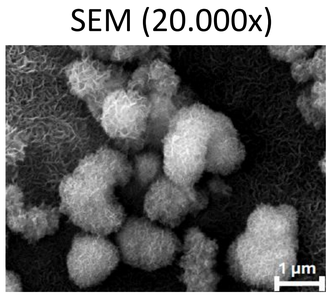
FTIR



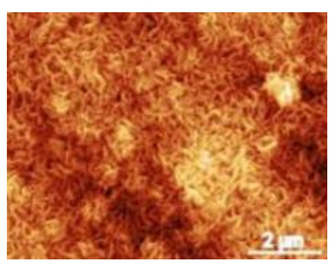
- **Morphology:** Spherical-shape aggregates with an average diameter of approximately 200–300 nm and a thickness of about 300 nm.
- **Crystallinity:** Thermal treatment enhances the crystallinity of the coatings.
- **Chemical composition**: The coatings are composed of HA. Compared with the synthetic HA reference, they exhibit less defined spectral bands, consistent with a lower degree of crystallinity.

Chemical Deposition: Biomimetic Deposition by SBF

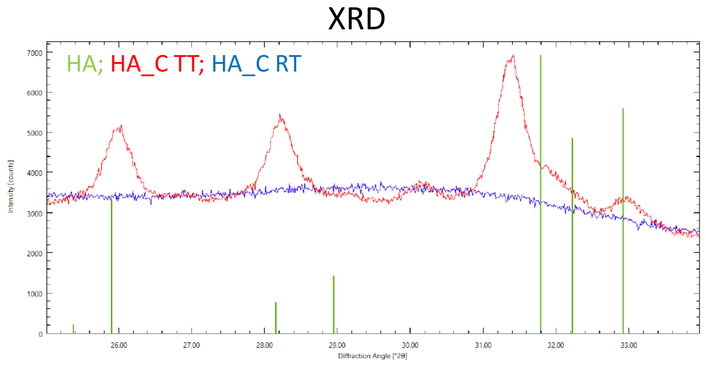
SEM (20.000x)



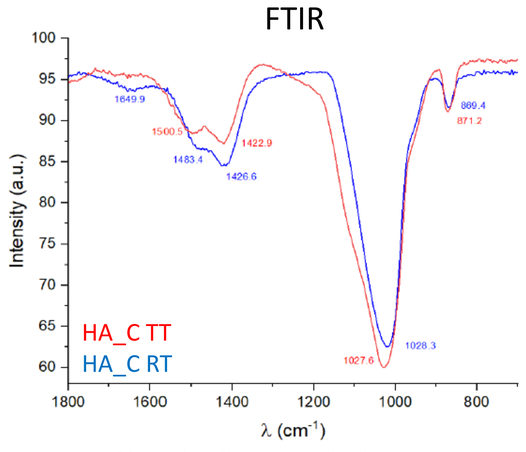
AFM



XRD



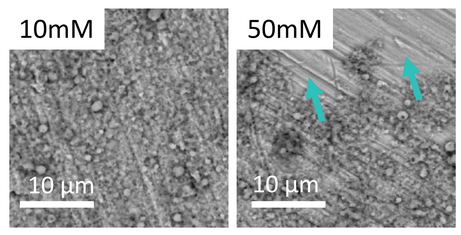
FTIR



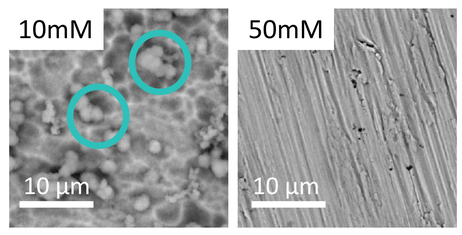
- **Morphology:** Needle-like morphology related to primary nucleation. Spherical features related to secondary nucleation layer with average diameter around 700-900 nm.
- **Crystallinity:** Thermal treatment enhances the crystallinity of the coatings.
- **Chemical composition**: The coatings are composed of HA. The thermal treatment promotes the crystallization with more defined and sharper bands.

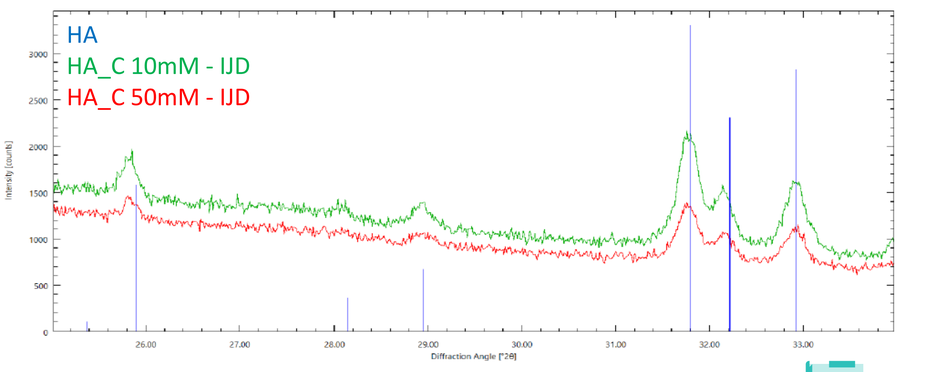
Functionalization with citrate

IJD

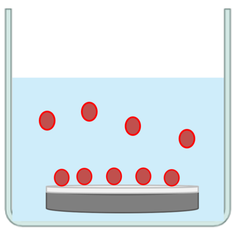


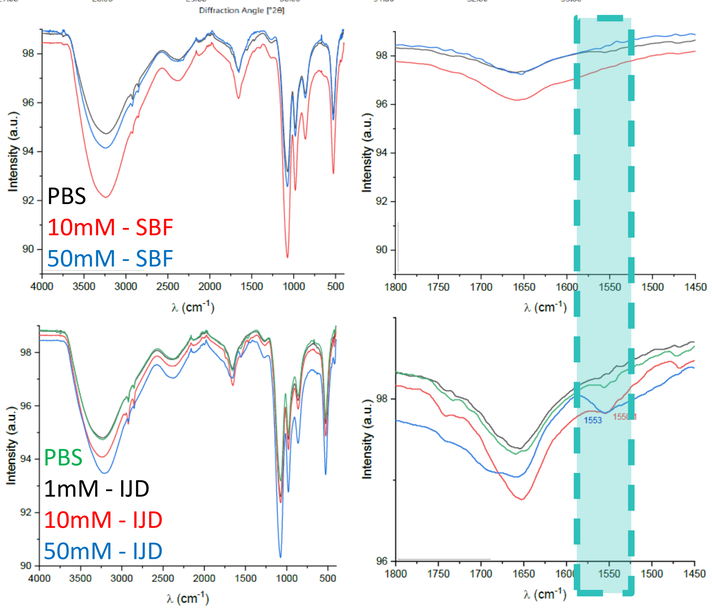
SBF





Citrate releasing in Phosphate Buffer Solution





- Biomimetic HA coating was almost completely dissolved, whereas the IJD-deposited HA coating remained largely intact. At higher citrate concentrations, the onset of delamination was observed (blue arrows).
- Citrate functionalization did not alter the chemical composition of the IJD-deposited HA coatings.
- For the IJD coatings, citrate was released into the PBS solution (band at 1550 cm^{-1}), confirming its successful incorporation into the coatings.

CONCLUSIONS

- IJD proved to be the most reliable coating technique, producing homogeneous, semicrystalline hydroxyapatite coatings on Ti6Al4V substrates starting from monetite.
- Citrate functionalization was successfully achieved on IJD coatings, with 10 mM representing the best compromise between effective adsorption and coating stability, while 50 mM induced partial coating delamination.
- Chemical deposition method showed limited effectiveness due to coating dissolution, preventing reliable citrate incorporation.
- PBS incubation confirmed the stability of IJD hydroxyapatite coatings, although quantitative evaluation of citrate retention requires further investigation.

FUTURE WORK

- Future work will focus on quantitative citrate detection (e.g., fluorescence-based assays).
- Optimization of the amount of citrate loading in the HA coatings.
- Early cytocompatibility assessment.
- Biological activity evaluation on mesenchymal stem cells to analyze the citrate-loaded HA coatings effects on their proliferation, colonization and osteogenic differentiations.