Influence of annealing temperature on nanostructured calcium phosphate coating synthesized by pulsed laser deposition under 1 Torr

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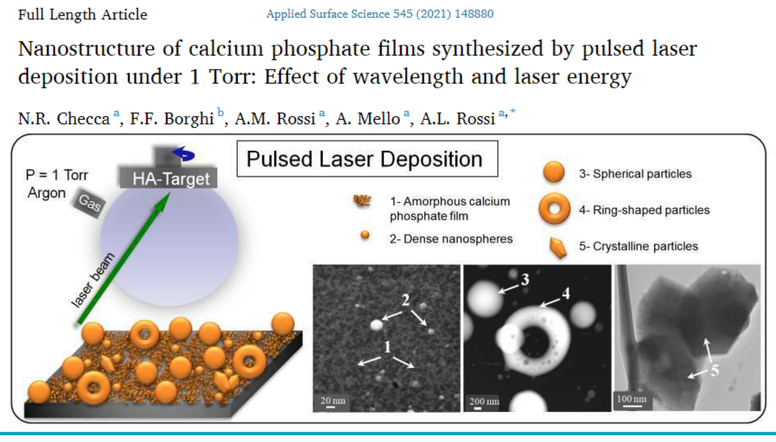
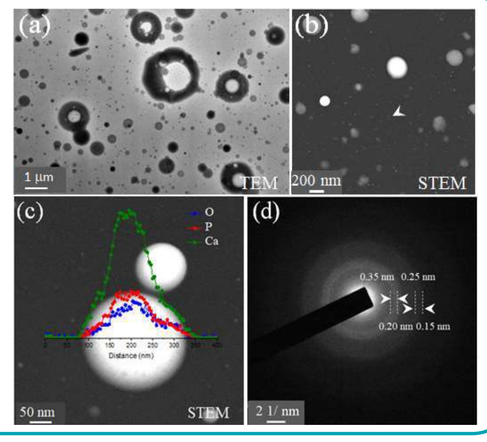
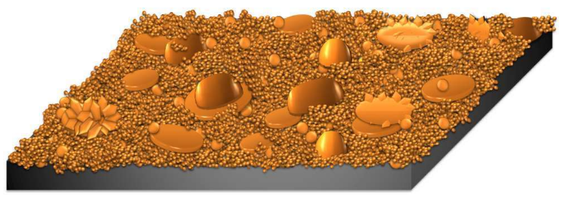
Hydroxyapatite (HA) has been widely applied as a coating material on metallic supports because it can induce bone regeneration and enhance biochemical interactions with biological systems, which promotes the regeneration of the bone. Nanostructured HA coatings can modify surface properties, even more, when they can generate a controlled porosity because this type of coating increases bioactivity, cytocompatibility, osteoconductivity, and osteogenesis. In this context, the pulsed laser ablation technique was used for the synthesis of HA coatings. Depositions were performed using a crystalline HA target at a background pressure of 1 Torr, laser wavelength of 532 nm, and pulse laser energy of 300 mJ. The coatings were deposited on Si substrate at room temperature (HA-1) and heated at 600 (HA-2), 1000 (HA-3), and 1200°C (HA-4). All coatings were studied using XRD, SEM, and EDS techniques. The as-deposited coatings were partially amorphous and had rough surfaces with a lot of droplets. Annealing was necessary to change the amorphous coating to a crystalline coating showing an interconnected network of HA nanoparticles. SEM indicated that the coating bottom is formed by nanoparticles and ultra-nanoparticles spherical. These two types of nanoparticles were studied by TEM in situ to elucidate the mechanism of porosity formation in annealed coatings. Lastly, for the crystallinity study, lamellas were prepared using FIB for analysis by TEM techniques. The EDS of the cross-section shows the diffusion of the substrate atoms as an effect of temperature, creating a calcium ions deficient layer while maintaining the hexagonal structure of HA.

Previous work

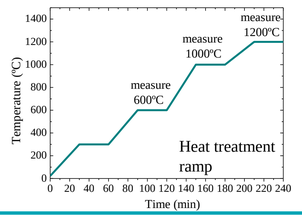




λ(nm)	E(mJ)	atm	P (Torr)	$d_{T\text{-}S}$ (cm)	t_d (min)
532	300	Argon	1	3	20



Sample	T(ºC)
HA-1	RT
HA-2	600
HA-3	800
HA-4	1200



XRD

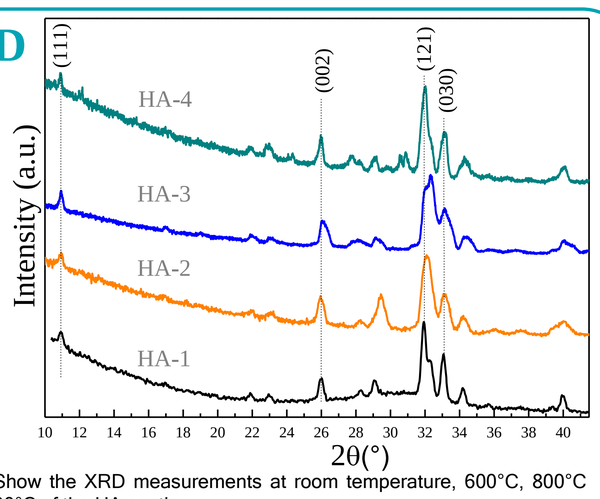


Fig 1. Show the XRD measurements at room temperature, 600°C, 800°C and 1200°C of the HA coatings.

SEM-EDS

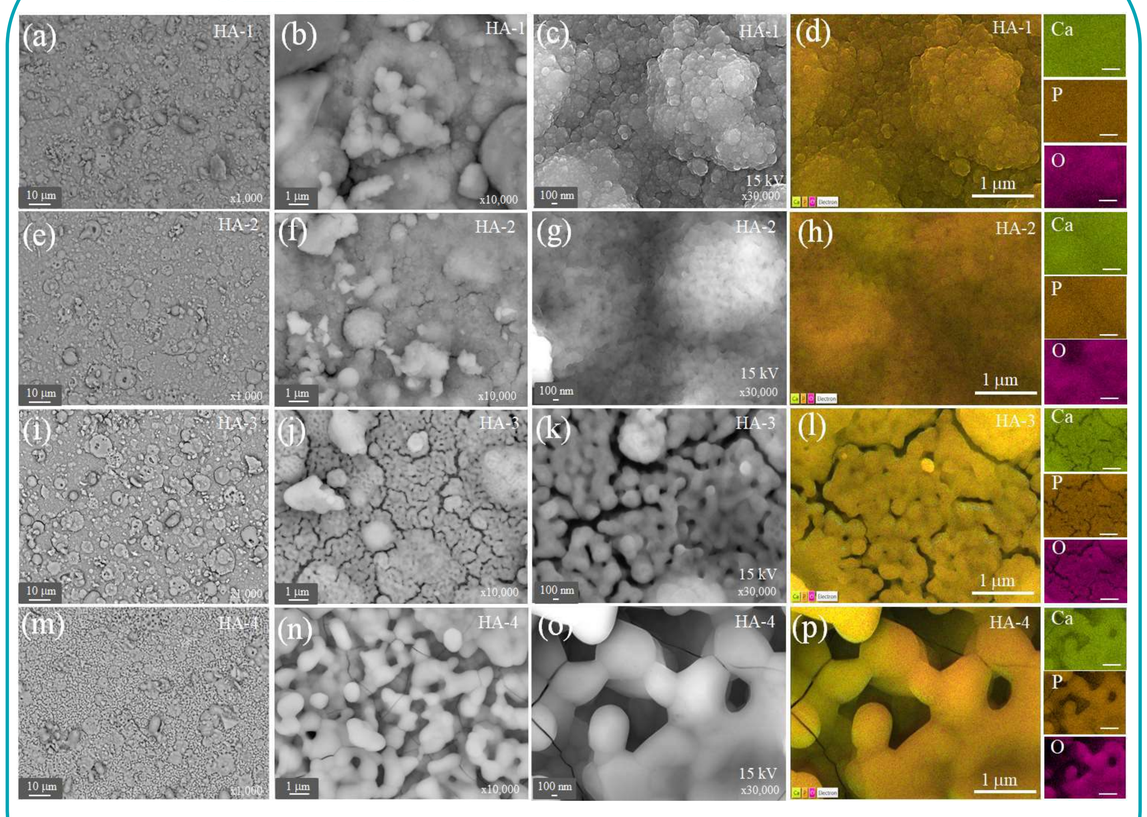
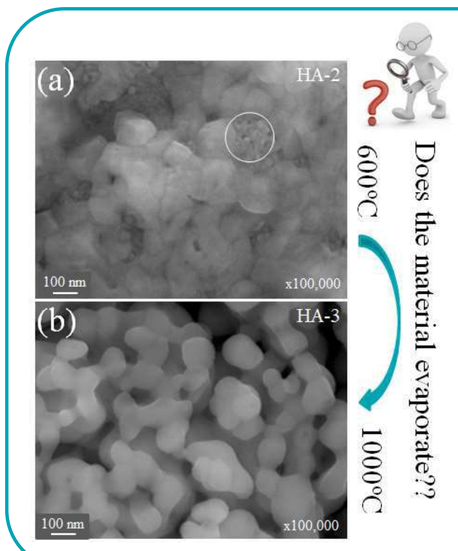


Fig 2. Top view of SEM and EDS images of HA coatings at room temperature, 600°C, 800°C and 1200°C at different magnifications.

TEM: IN SITU



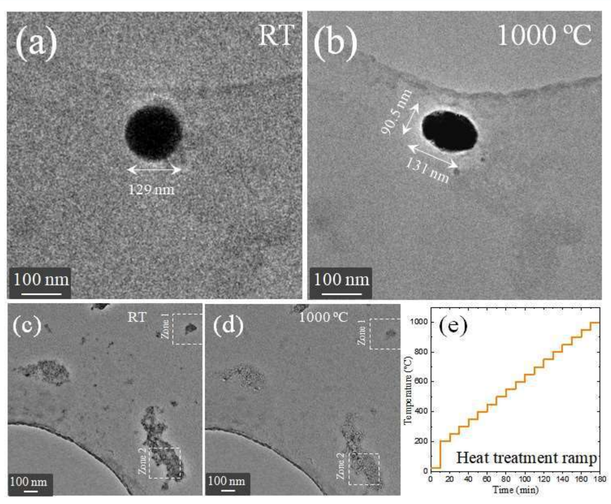


Fig 3. TEM Images of nanoparticles and ultra-nanoparticles as deposited before and after reaching 1000ºC in 180 min.

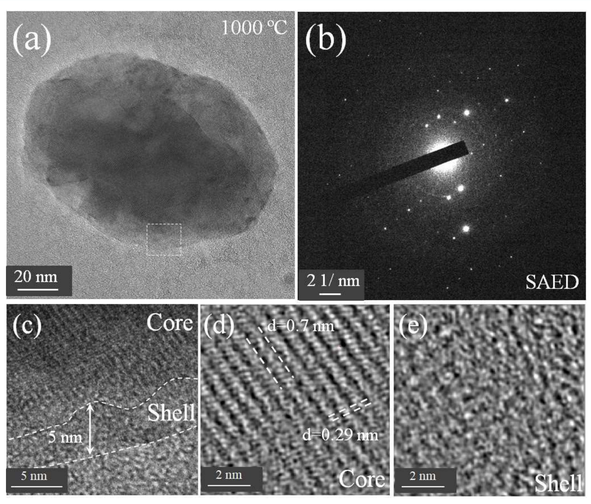


Fig 4. TEM Images of nanoparticles after reaching 1000ºC.

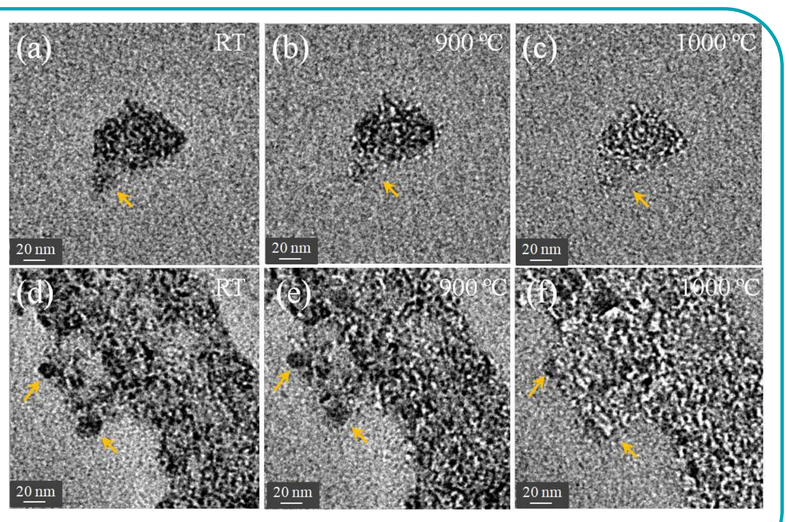


Fig 5. TEM Images of the ultra-nanoparticles before, during, and after reaching 1000°C.

FIB: TEM

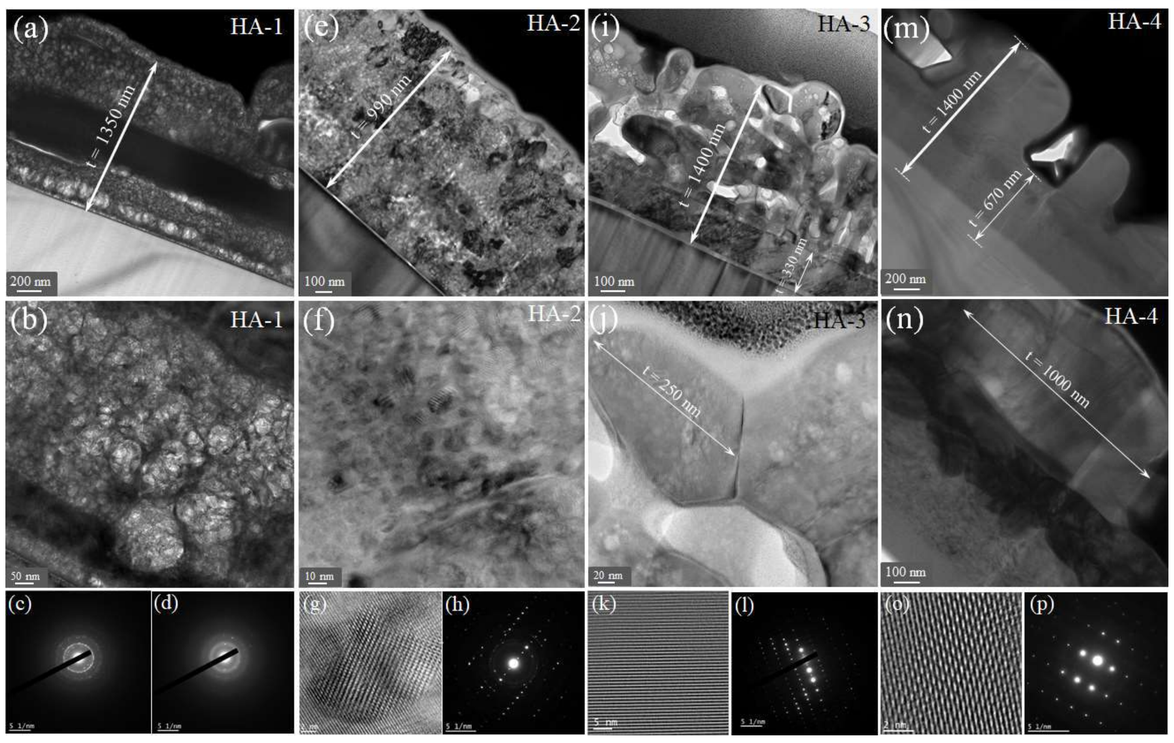
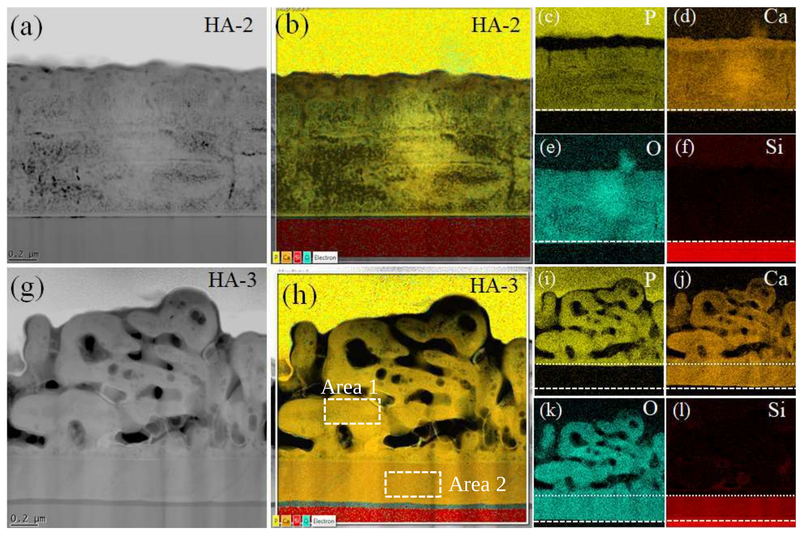


Fig 6. TEM images from the cross-section of the HA coatings at room temperature, 600°C, 800°C, and 1200°C.

STEM-EDS



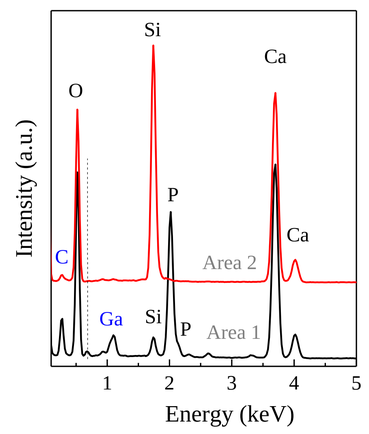


Fig 7. STEM images and EDS mapping from the cross-section of the HA coatings at 600°C and 800°C with their respective elementary maps.

CONCLUSION

- We successfully synthesized by PLD + heat treatment a porous nanostructured coating composed of HA particles.
- TEM in situ shows that the material of the ultra nanoparticles is metastable and evaporates at temperatures between 900 and 1000ºC

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