Ion exchange process was carried out by immersing the coated samples To achieve ion exchange, the coated samples were immersed in the copper-based solution for a total time of 15 minutes

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Copper doped hydroxyapatite-based coatings for medical applications

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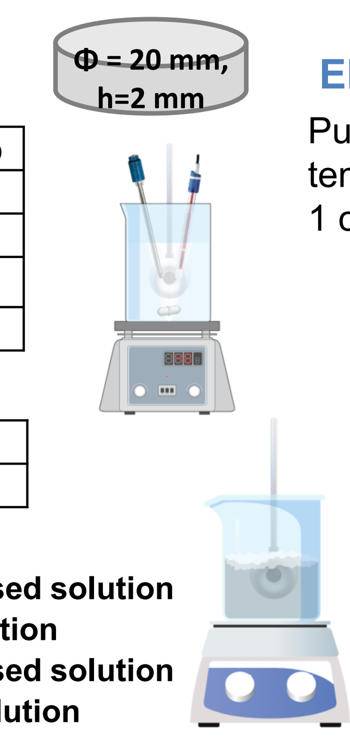
INTRODUCTION & AIM

The success of an implant depends on its osseointegration, while its long-term survival is determined by its resistance to bacterial infections. Titanium, commonly used for its mechanical properties and corrosion resistance, but has limitations regarding its osteointegration and antibacterial efficiency. The objective of the present study is to functionalize the titanium surface with hydroxyapatite, which has been demonstrated to stimulate bone regeneration, and to doped it with copper, which is known to possess antibacterial properties.

METHOD

Ti substrate as discs (SiC 120 – 800 grit)



Electrochemical deposition

Sample codification		nHAp	cHAp
Electrolyte composition (mM)	$Ca(NO_3)_2 \cdot 4H_2O$	10	-
	$CaCl_2 \cdot 2H_2O$	-	10
	$NH_4H_2PO_4$	6	
Ca/P Ratio		1.67	

Ionic exchange

Solution	0.01 mM $Cu(NO_3)_2$	nHAp-Cu
	0.01 mM $CuCl_2$	cHAp-Cu

Sample codification

- cHAp - hydroxyapatite obtained from chloride salt-based solution
- cHAp -Cu – cHAp doped with Cu by using a CuCl solution
- nHAp – hydroxyapatite obtained from nitrates salt-based solution
- nHAp-Cu – nHAp doped with Cu by using a $CuNO_3$ solution

Electrochemical parameters

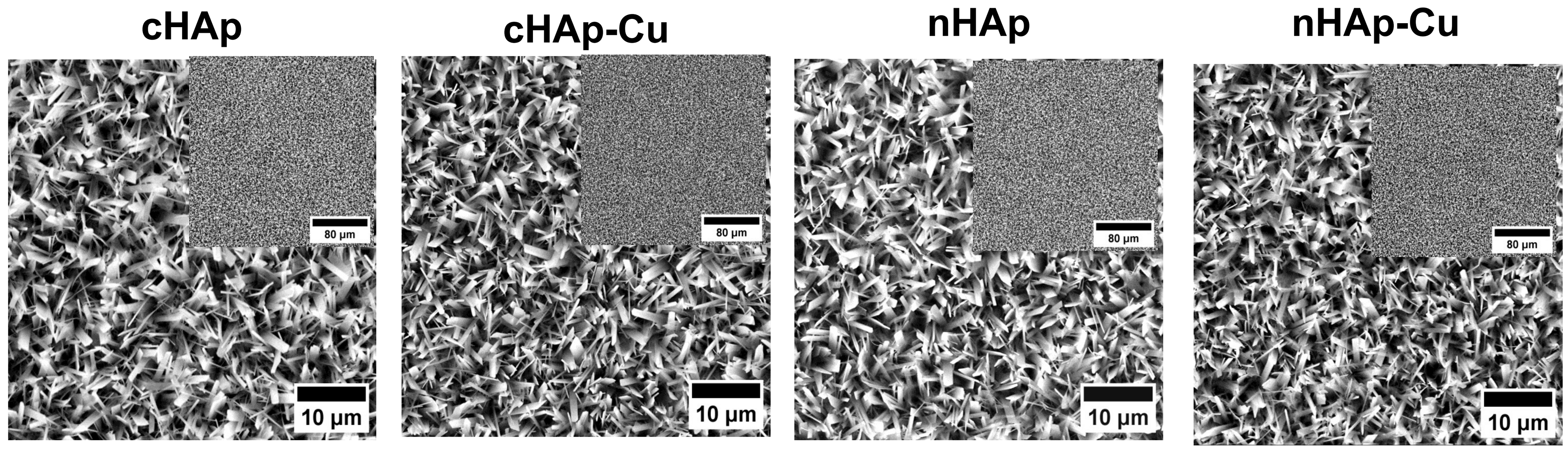
Pulsed galvanostatic temperature of 75 ℃,
1 cycle:
- i_{ON} of −0.85 mA/cm² for t_{ON} = 1 s
- i_{OFF} of 0 mA/cm² for t_{OFF} = 1 s
- 900 cycles

Ionic exchange parameters

The coated samples were immersed in the copper-based solution for a total time of 15 minutes (10 min. under continuous stirring, 5 min static)

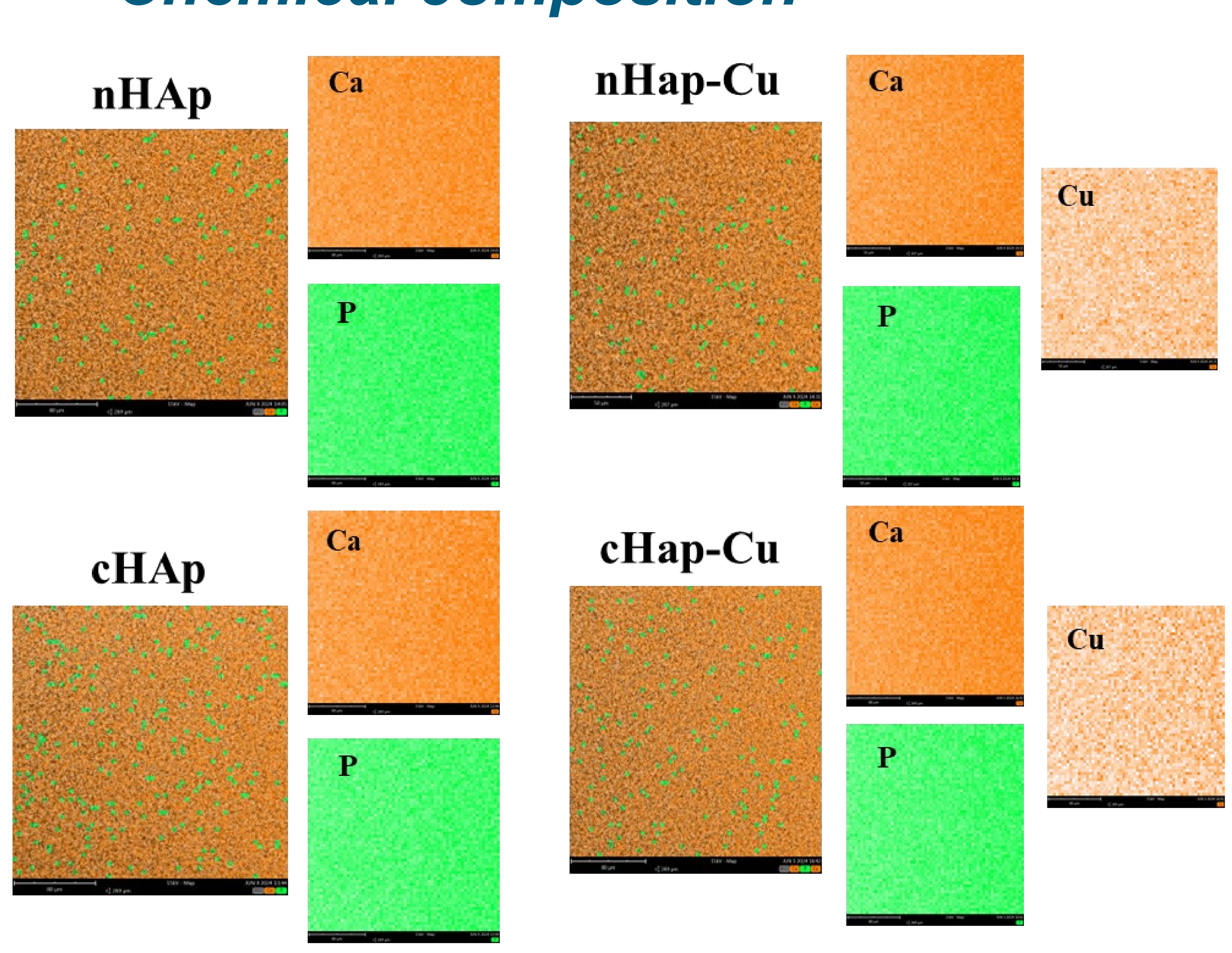
RESULTS & DISCUSSION

Morphology

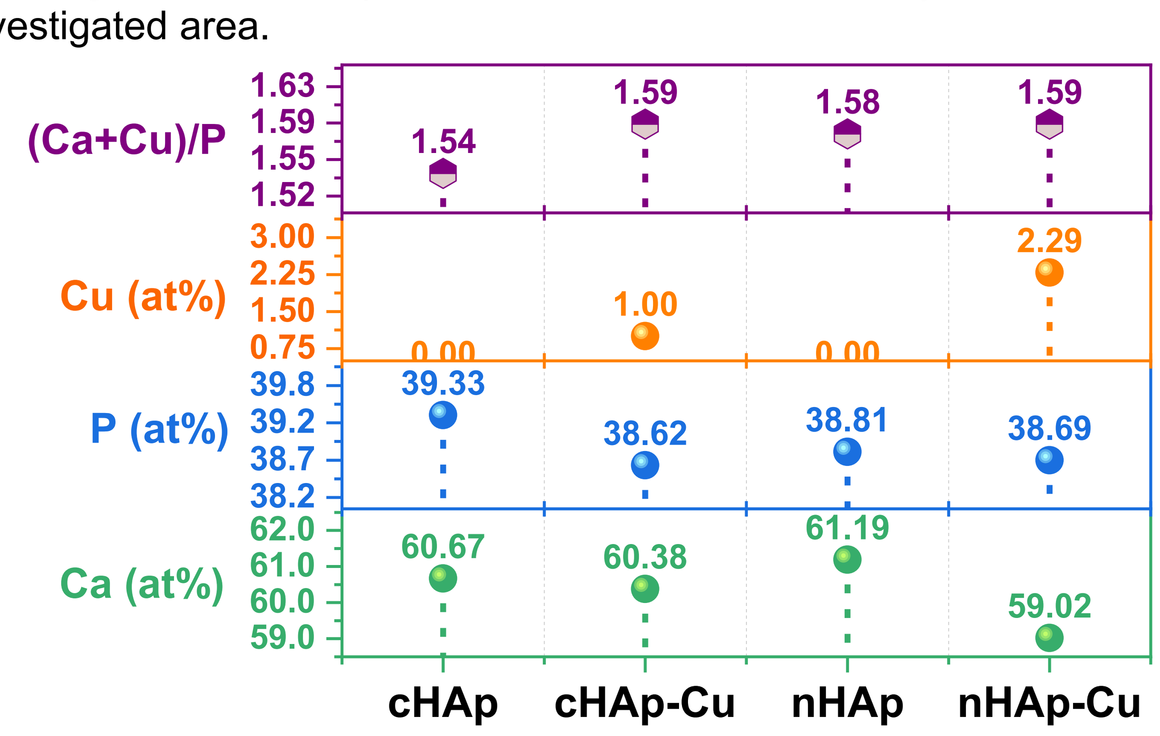


According to the SEM images it can be noticed that all coatings are composed of ribbon-like crystals, very thin and narrow which are grown perpendicular to the cp-Ti surface, irrespective of the electrolyte type. The crystallization direction is characteristic of the electrochemical deposition technique. Regardless of electrolyte's nature, the substitution of Cu into HAp structure conducted to a decrease in ribbons like crystals, these being thinner and denser.

Chemical composition

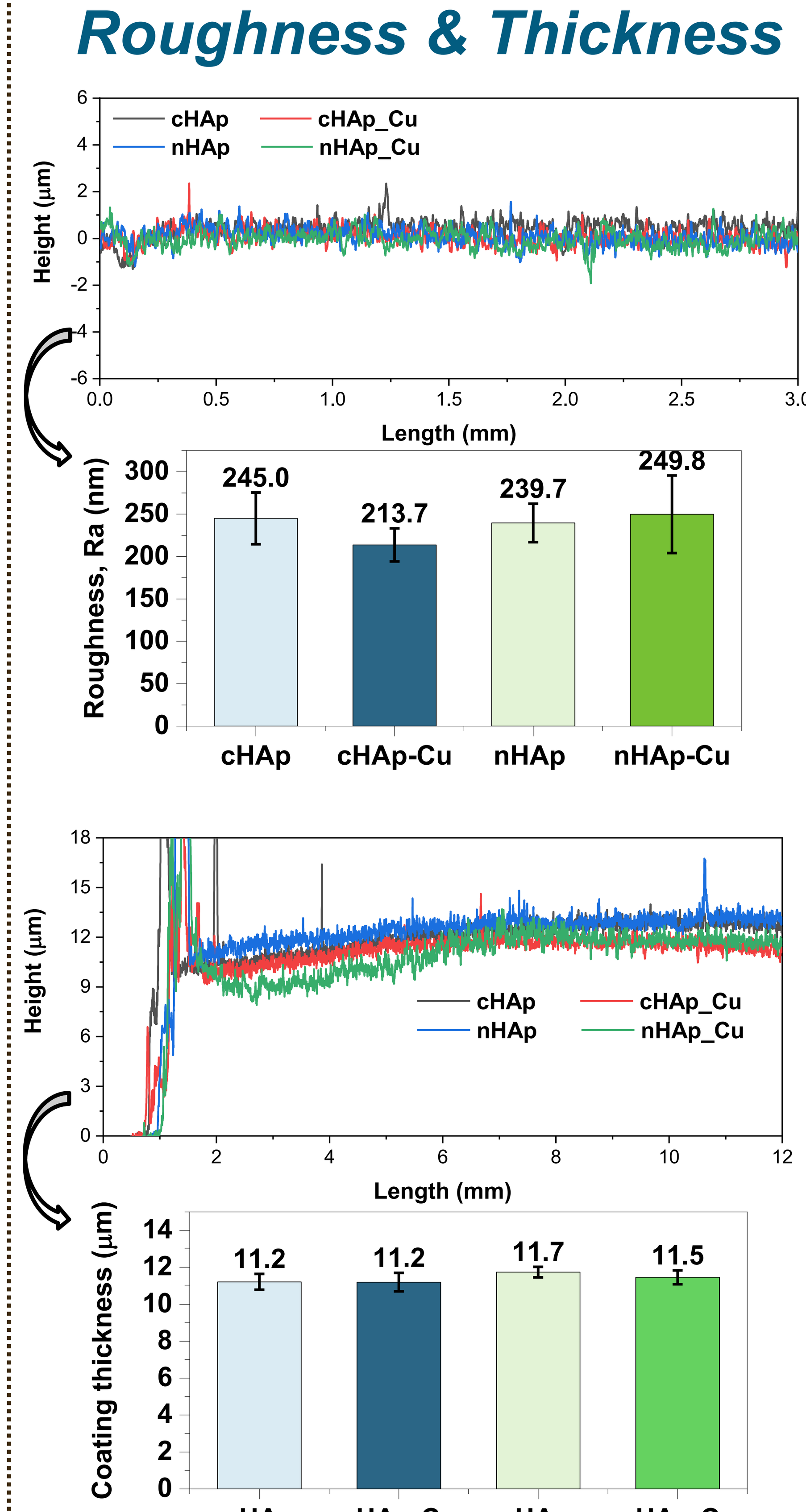


The EDS analysis has confirmed the presence of the characteristic elements of hydroxyapatite (Ca, P, O) as well as copper (Cu) in the ion exchange treated samples. All elements are uniformly distributed on the investigated area.



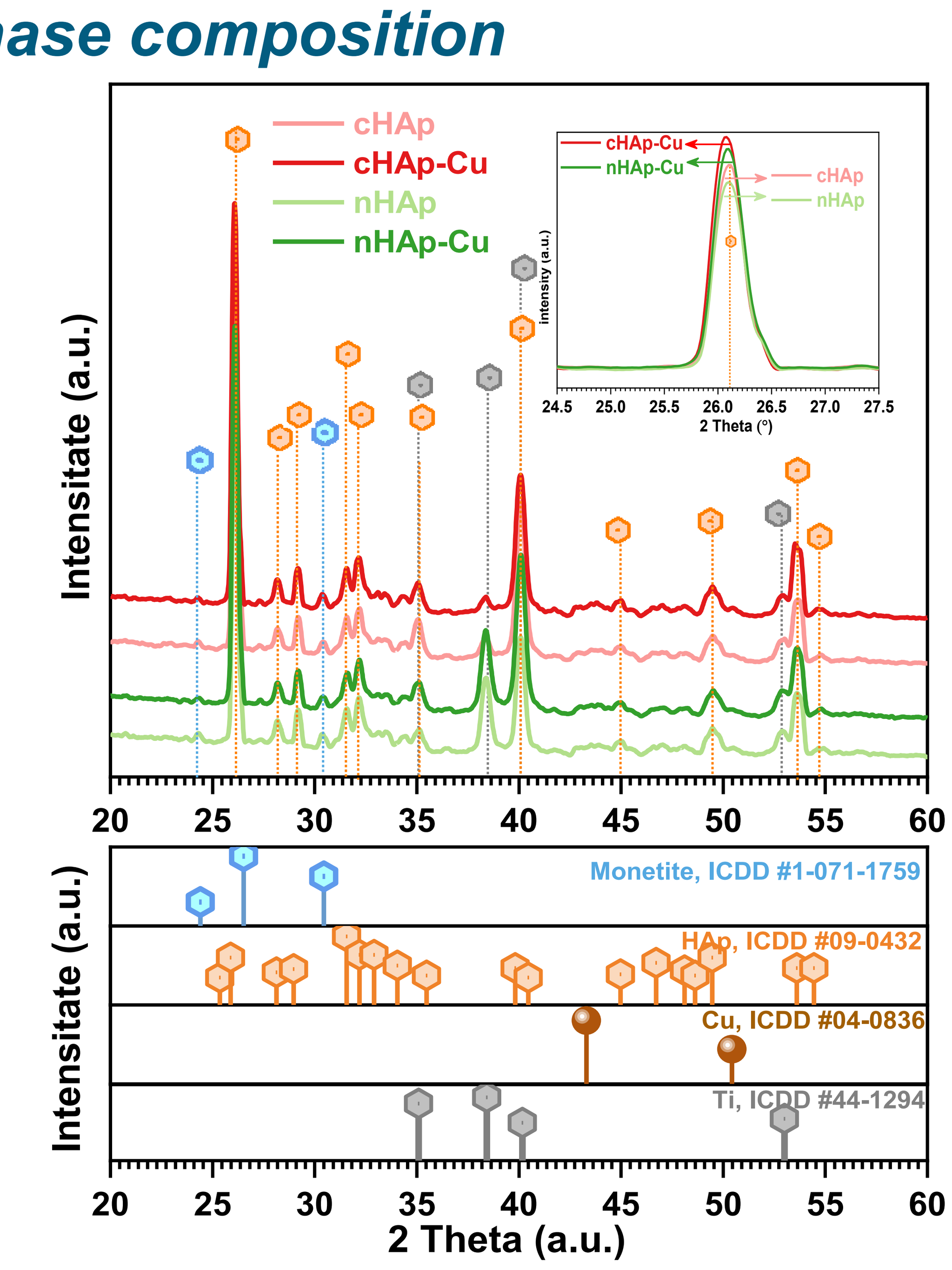
The (Ca+Cu)/P ratio have registered values close to the stoichiometric (1.67) one of natural HAp irrespective of the electrolyte type (chlorides vs nitrates), with larger values beind noted after the addition of Cu, with values of 1.59.

Roughness & Thickness



Irrespective of the electrolyte type, the average roughness (Ra) values indicated a moderate increase in copper doped coatings compared to undoped ones. Increased roughness is considered beneficial for cell adhesion and favors osseointegration. In terms of thickness, it can be noted that all coatings registered values between 11.2 and 11.7 µm.

Phase composition



Crystallite dimension

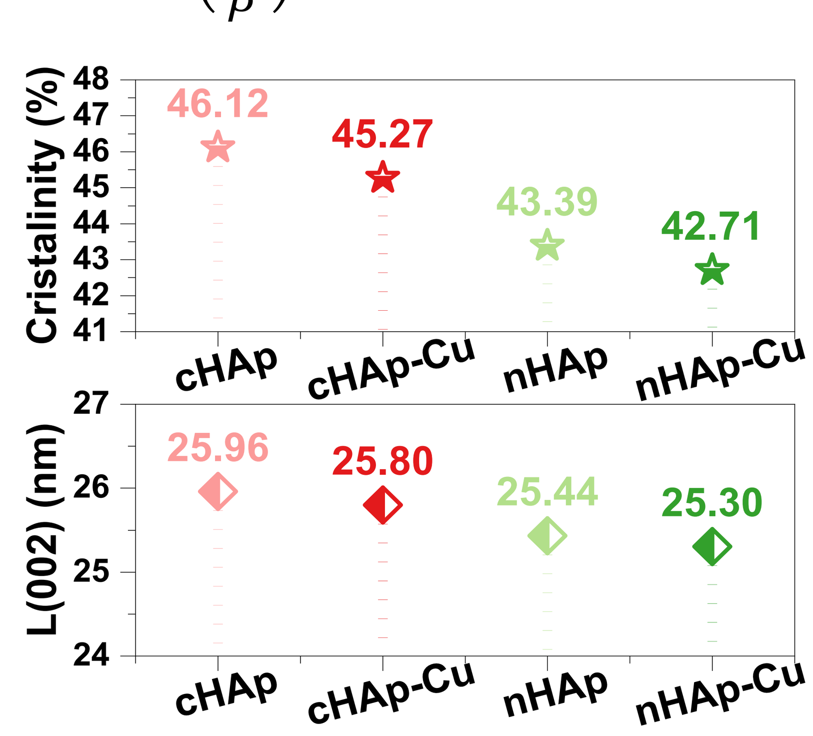
$$L_{(002)} = \frac{0.9\lambda}{\beta cos\theta}$$

where 0.9 is Scherrer constant value, λ is the wavelength of X-ray employed, Cu Kα =0.154 nm, β is the full width of the diffraction peak at half maximum, and θ is the diffraction angle

Crystallinity

$$\chi_c = \left(\frac{K_A}{\beta}\right)^3$$

where K_A is a constant found equal to 0.24 for HAp, and β is the FWHM of refection (002) in degrees



X-ray diffraction confirmed the presence of hydroxyapatite according to ICCD # 09-1432, with peak positions and intensities unchanged after copper doping with respect to type of electrolyte which has been used. In terms of crystallinity and crystallite dimension, it was noted that the coatings obtained from chloride salts present higher values than the ones obtained from the nitrate ones.

CONCLUSION

In conclusion, it can be stated that hydroxyapatite-based coatings obtained through electrochemical techniques can be successfully doped with copper by using the ion exchange method, from both types of electrolytes, namely chloride and nitrate ones.