

# Functionalized surface of a ceramic carbonated apatite substrate with an antibacterial $\alpha$ -tocopheryl phosphate organic layer

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## INTRODUCTION & AIM

The water-soluble derivative of vitamin E,  $\alpha$ -Tocopheryl phosphate ( $\alpha$ -TP), has shown antibacterial and pro-osteogenic potential. On chemically treated Ti6Al4V,  $\alpha$ -TP could be immobilized through  $\text{Ca}^{2+}$ -mediated interaction with its phosphate head group [1].

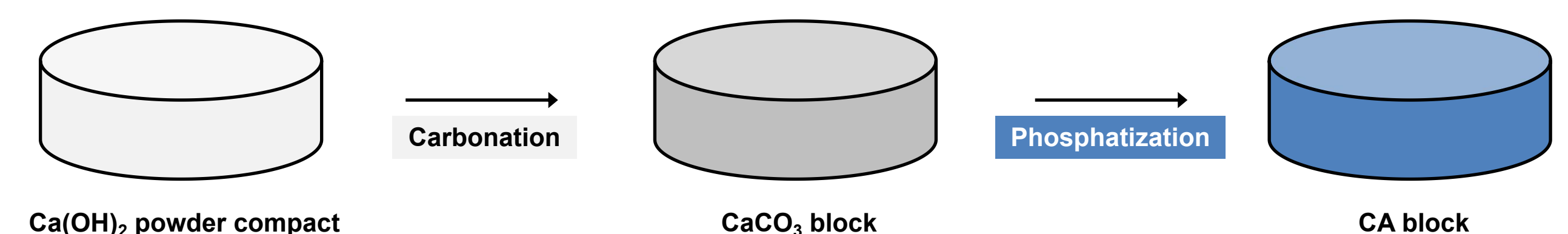
Carbonated apatite (CA), a close synthetic analogue of the human bone mineral, contains calcium, phosphate, and carbonate ions in its crystalline lattice and can be resorbed by osteoclasts and replaced by newly formed bone [2, 3].

Since  $\text{Ca}^{2+}$  appears to bridge  $\alpha$ -TP to the surface of treated Ti alloys, we hypothesized that Ca-rich surface of CA could intrinsic provide anchoring sites for  $\alpha$ -TP, possibly enabling the formation of an antibacterial and bioresorbable synthetic bone graft.

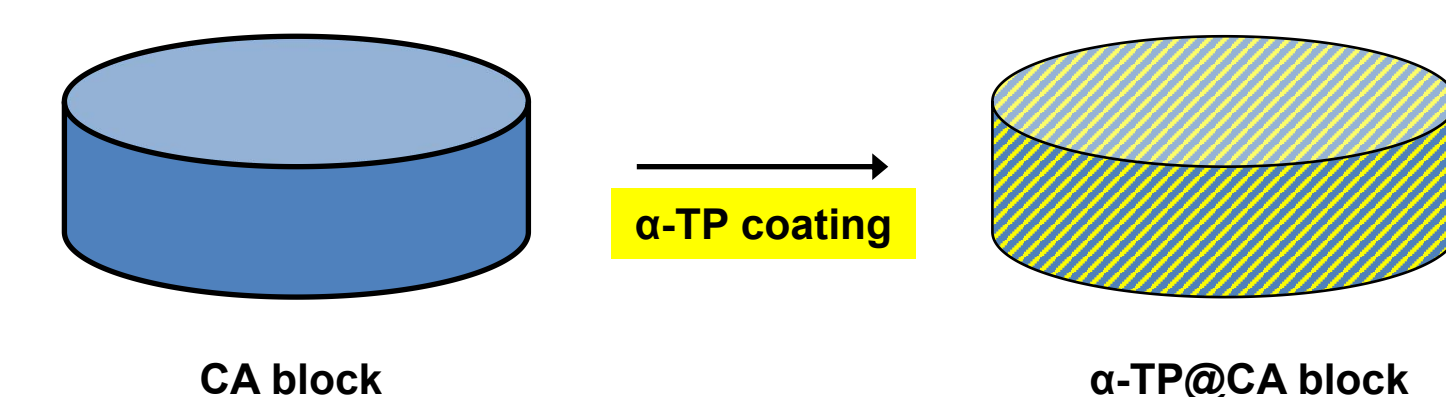
This preliminary study aimed to determine whether  $\alpha$ -TP can be coated onto CA substrates and whether the resulting coating remains stable after attempted removal.

## METHOD

Substrate synthesis:  $\text{Ca}(\text{OH})_2$  powder compacts were pressed at  $\sim 200$  MPa and carbonated in water-saturated  $\text{CO}_2$  atmosphere to obtain  $\text{CaCO}_3$  blocks. CA blocks were achieved by dissolution-precipitation in 0.1 mol/L  $\text{Na}_2\text{HPO}_4$  at  $80^\circ\text{C}$  for 7 days.

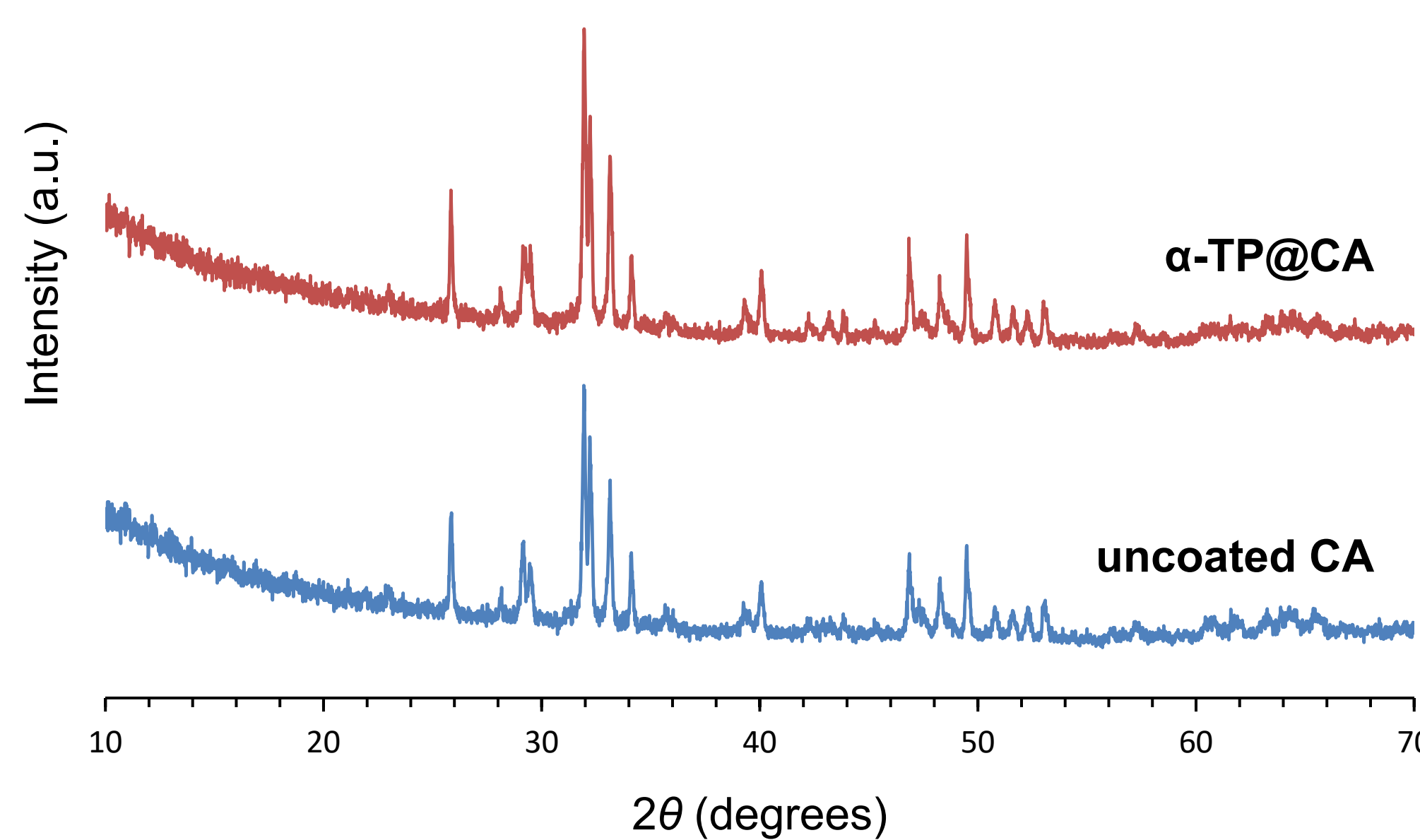


Coating synthesis: CA blocks were immersed into  $\sim 10$  mmol/L  $\alpha$ -TP solution at room temperature for 3 h, then dried in air without rinsing to obtain  $\alpha$ -TP-coated CA ( $\alpha$ -TP@CA).

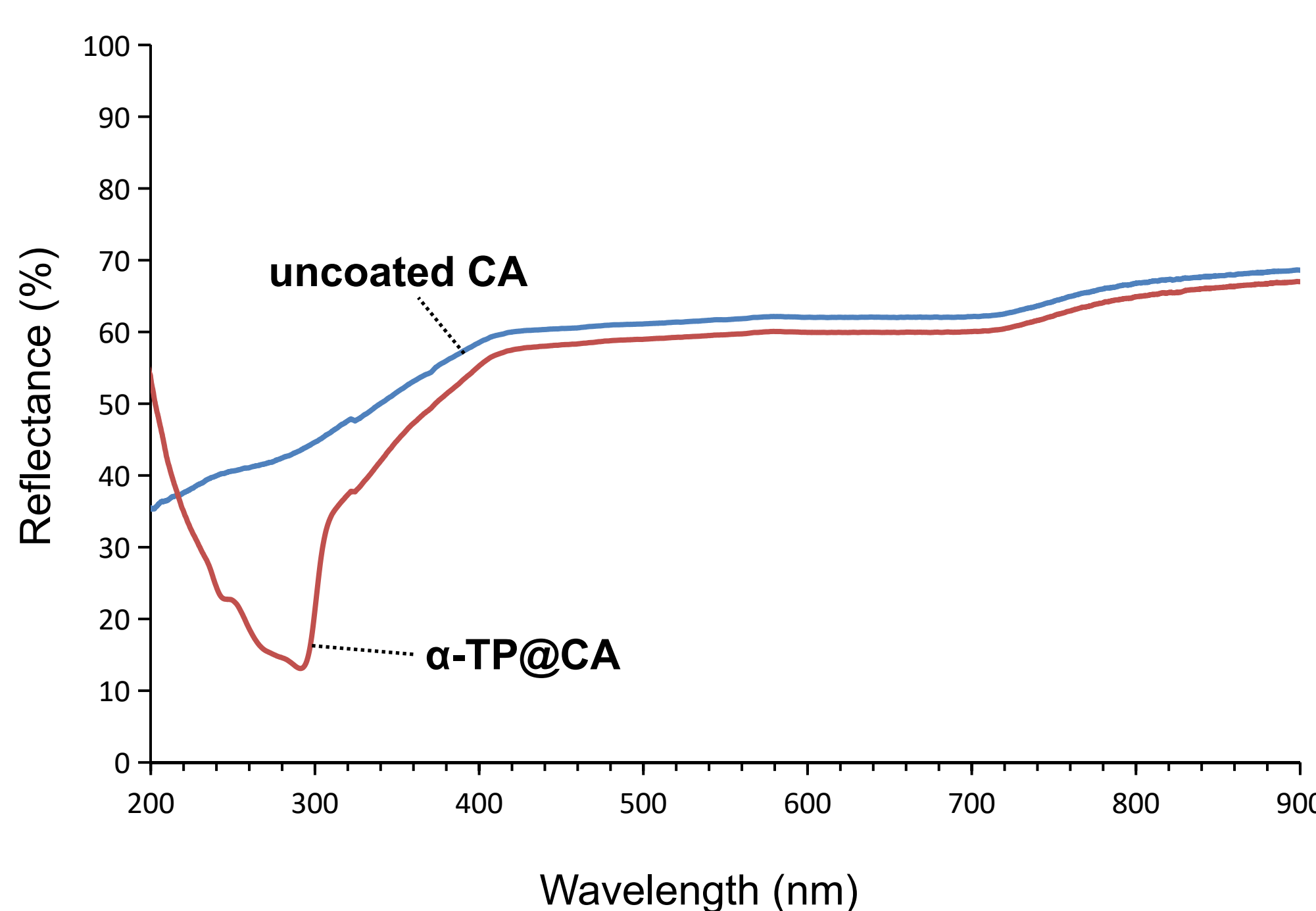


## RESULTS & DISCUSSION

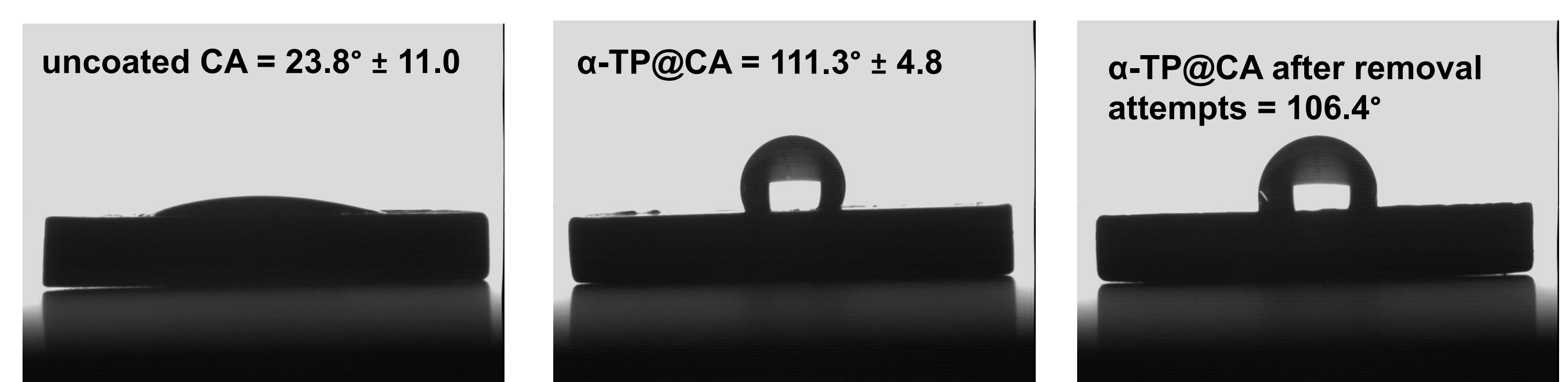
XRD confirmed the apatitic formation, with characteristic (211) and (300) reflections at  $\sim 31.9^\circ$  and  $33.1^\circ$ , respectively. No  $\alpha$ -TP-related amorphous halo was detected, possibly indicating that the coating was below the detection limit of XRD.



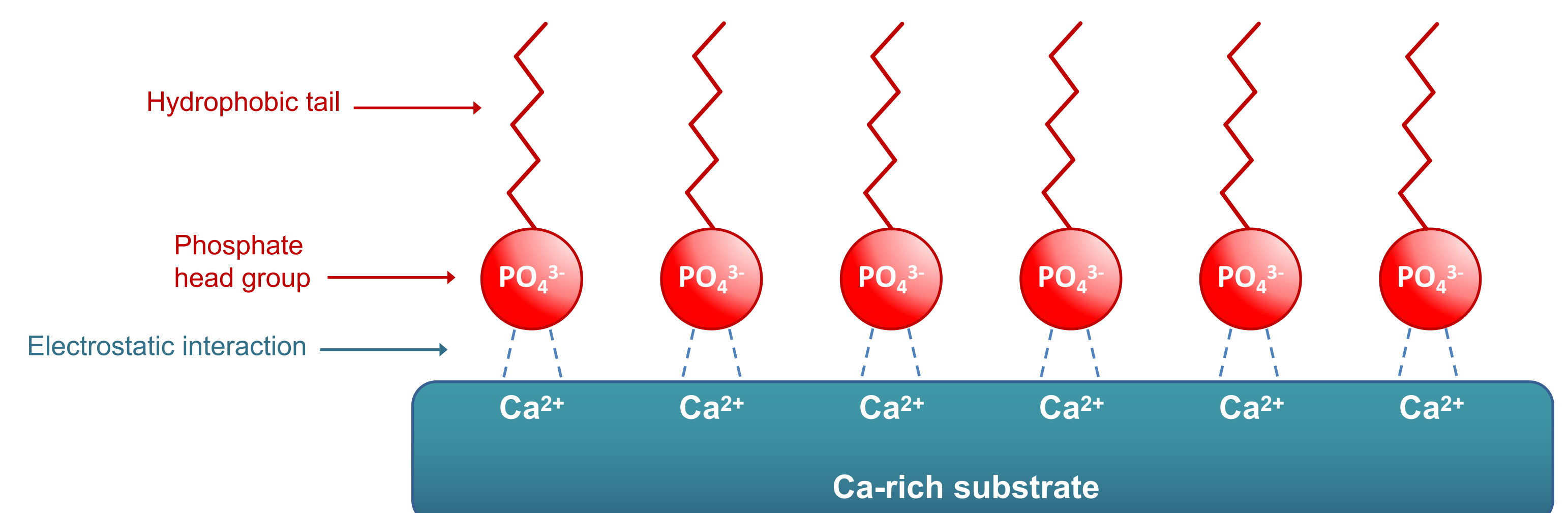
UV-vis analysis showed the typical high-reflectance profile of uncoated white CA, whereas  $\alpha$ -TP@CA exhibited a UVB-region feature around 280 nm, consistent with  $\alpha$ -TP presence on the surface.



Water contact angle (WCA) confirmed the highly hydrophilic character of CA. In contrast,  $\alpha$ -TP@CA became strongly hydrophobic, suggesting outward exposure of hydrophobic  $\alpha$ -TP moieties. Moreover, after ultrasonication in acetone or immersion in 25% ammonia solution, WCA remained  $>100^\circ$ , indicating a persistent hydrophobic  $\alpha$ -TP surface layer on the CA substrate.



We hypothesize that exposed  $\text{Ca}^{2+}$  sites on the CA surface coordinate the phosphate head group of  $\alpha$ -TP, favoring a predominantly phosphate-down/tail-out molecular orientation. This partially contrasts with Gamna et al., who reported hydrophobic  $\alpha$ -TP-functionalized Ti6Al4V ( $\sim 80^\circ$  WCA) but hydrophilic  $\alpha$ -TP-coated Ti6Al4V ( $\sim 40^\circ$  WCA), attributed to outward-facing phosphate groups in a thicker coating. In the present CA substrate, the persistent hydrophobicity suggests preferential stabilization of phosphate-down  $\alpha$ -TP molecules, limiting the formation or retention of an outward phosphate-exposed layer.



## CONCLUSIONS

$\alpha$ -TP was successfully coated onto CA while preserving the apatitic phase. UV-vis and WCA results indicated  $\alpha$ -TP presence on the surface, with hydrophobicity persisting after aggressive removal attempts. These findings suggest that CA can anchor  $\alpha$ -TP via interactions between surface  $\text{Ca}^{2+}$  sites and phosphate head groups. However, this strong hydrophobicity may impair protein adsorption, cell attachment, and bone healing, indicating the need to optimize coating stability while restoring cytocompatible wettability.

## FUTURE WORK/ REFERENCES/ACKNOWLEDGMENT

- References:
- [1] Gamna et al. *Applied Surface Science*, 2023, 619, 156681.
  - [2] Hayashi et al. *Materials Today Bio*, 2019, 4, 100031.
  - [3] Freitas et al. *Journal of Biomedical Materials Research Part A*, 2022, 110, 1278-1290.

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- Future work:
1. Improve wettability to cytocompatible levels
  2. Expand chemical and biological characterization